PEDRO DEYRIEUX CENTENO OGANDO DOS SANTOS

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Heavy metals removal in dual media filters

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Orientador: Prof. Doutora Leonor Amaral, FCT/UNL
Co-orientador: Eng.ª Diana Brandão, TU Delft

Júri:

Presidente: Prof. Doutor António Pedro de Macedo Coimbra Mano
Arguente(s): Prof. Doutora Rita Maurício Rodrigues Rosa
Vogal(ais): Prof. Doutora Leonor Miranda Monteiro do Amaral

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«*You can't build a reputation on what you are going to do…*»

Henry Ford

(1863-1947)

I dedicate this MSc Thesis to my parents, my family, my girlfriend and my friends

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RESUMO

O presente estudo pretendeu investigar mecanismos de remoção físico-químicos de metais pesados (nomeadamente de precipitação) de águas residuais tratadas da ETAR de Harnaschpolder, localizada no Sul da Holanda, para que seja possível a produção de dois tipos de águas de qualidade diferentes: águas «superficiais» e águas para a irrigação em estufas.

Para tal, foram construídos dois filtros de dupla camada na estação piloto da ETAR de Harnaschpolder. Após montagem e operação inicial dos filtros, concentrações específicas de metais pesados (Cd, Cu, Ni e Zn) foram doseadas a montante do processo, e estudou-se a remoção dos metais pesados. Num projecto paralelo a este, foi também estudada a remoção destes metais pesados através da inoculação de bactérias específicas.

Curvas de solubilidade foram construídas, utilizando o software *PHREEQc*, para simular as condições existentes nos filtros (pH, temperatura, alcalinidade, etc.) e calcular a probabilidade de precipitação dos metais pesados quando sujeitos as estas condições, de forma a confirmar a remoção (ou a não remoção) destes metais.

Os resultados tanto das experiências como da simulação sugerem que a precipitação de metais pesados (sobre a forma de hidróxidos, carbonetos e carbonatos, cianetos, sulfatos e sulfitos) não tenha ocorrido, devido às condições inerentes dos filtros. Os resultados sugerem ainda que outros mecanismos estejam envolvidos na remoção destes metais, possivelmente adsorção e/ou quelação.

Palavras-chave: metais pesados, filtração terciária, águas residuais tratadas, reutilização de águas

ABSTRACT

The purpose of this study was to investigate physicochemical mechanisms for the removal of heavy metals from the effluent of Harnaschpolder's WWTP Pilot Installation in the South of Netherlands. This effluent is partially submitted to tertiary treatment in a water reuse pilot which aims the production of water for two different end-uses: crop irrigation in greenhouses and surface-type water.

Tertiary filters were mounted and started up at the reuse pilot and specific concentrations of heavy metals were dosed in the filters. Removal efficiencies were then calculated after the end of the experiments. As a parallel research project, the removal of HM was also carried out by inoculating selected bacteria (biosorption).

Solubility curves were calculated for the dosed heavy metals (Cd, Cu, Ni, Zn) using PHREEQc programme, to predict if heavy metal precipitation occurred in the filters (using the same experimental data: temperature, pH , alkalinity, etc.).

Results show that physicochemical precipitation was not the primary removal mechanism for heavy metals. The results suggest that other mechanisms such as adsorption and/or chelation may be involved in the removal of these species.

Keywords: heavy metals, tertiary filtration, treated urban wastewater, water reuse

LIST OF ABBREVIATIONS AND SYMBOLS

Cd – Cadmium
CdCO3 – Cadmium carbonate
Cd(OH)2 – Cadmium hydroxide
cmWC – centimeters of Water Column
Cr – Cromium
Cu – Copper
$CuCO_3$ – Copper carbonate
$Cu(OH)_2$ – Copper hydroxide
COD – Chemical Oxygen Demand
CSF – Continuous Sand Filtration
DMF – Dual Media Filter
FFFM (or 3FM) – Flexible Fiber Filter Module
Hg – Mercury
HM – Heavy Metal(s)
HNP – Harnaschpolder
HRT – Hydraulic Retention Time
ICP-MS – Inductively Coupled Plasma – Mass Spectrometry
MeOH – Methanol
MERESAFIN – MEtal REmoval by SAnd Filtration INoculation
MF – Micro Filtration
MMSF – Multi Media Sand Filtration
MS – Mother Solution (of heavy metals)
MTR – Maximum Tolerable Risk
NF – Nanofiltration
Ni – Nickel
$NiCO_3$ – Nickel carbonate

$Ni(OH)_2$ – Nickel hydroxide

NO_3 – Nitrate

NTU – Nephelometric Turbidity Units

NW4 – «*Notavierde Water 4*»: Fourth National Policy Document on Water Management

Pb – Lead

PHREEQc – Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations

RO – Reverse Osmosis

RPM – Revolutions Per Minute

SBBR – Static Bed Bio-Reactor

SWL – Supernatant Water Level

Tr – Filter run time

TSS – Total Suspended Solids

UF – Ultra Filtration

VRO – Vertical Reverse Osmosis

WWTP – Wastewater Treatment Plant

Zn – Zinc

$Zn(CO_3)$ – zinc carbonate or «*smithsonite*»

$Zn(CO_3).H_2O$ – zinc carbonate monohydrated

ZnS – zinc sulfite or «*spharelite*»

$Zn(OH)_2$ – zinc hydroxide

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This thesis describes the work done by the author in the department of Water Management in the Civil Engineering and Geosciences building (CiTG), at the Technical University of Delft in the Netherlands. It was supervised there by Diana Brandão in the scope of a project research on water reclamation, under the promotion of Professor ir. Jules van de Lier. This MSc thesis was also under the supervision of Professor Leonor Amaral, from the Environmental Engineering Department at the Faculty of Sciences and Technology of the New University of Lisbon (FCT/UNL), in Portugal under the European Mobility Programme «*Erasmus Long Life Learning*».

This project was included in a greater project called «*Delft Blue Water*» (www.delftbluewater.nl), a consortium of five companies: Evides, Rossmark, Veolia, Delfluent Services and Delfland and the University of Delft, whose primary goal was to produce two types of water: surface-type water and irrigation water for the greenhouses of the Delft region.

1. INTRODUCTION

1.1 General Overview

Water is a necessity for both individual and community well being. Factors as the growth of the world's population and climate change contribute to an increase of the demand for fresh water sources. As a result, many countries have been forced to reassess the long-term reliability of their water supply systems and consider other solutions such as the reuse of treated wastewater, combining the most efficient and effective technologies for wastewater treatment (Janosova *et al.*, 2006).

Types of water reuse

In general, wastewater can be reused through two major sources: the central wastewater treatment plants (*i.e.* WWTPs) and decentralized in-house grey-wastewater or on-site wastewater treatment facilities (Uitto and Biswas, 2000).

Centralized reclaimed wastewater is widely used for non-potable applications. The current major ones include agricultural irrigation, industrial uses, municipal water uses and private water uses (*e.g.* toilet flushing and garden watering). Other applications are also in practice such as environmental protection (*e.g.* creating artificial wetlands, enhancing natural wetlands and sustain stream flows), groundwater recharge (*e.g*. salt-water intrusion control, subsidence control and groundwater replenishment) as well as potable reuse (Anderson *et al*., 2001, Chu *et al*., 2004, Angelakis *et al*., 1999).

The Pilot Plant at the Harnaschpolder WWTP plans to produce water with a quality equivalent to surface water and irrigation water for the local producers in the near future.

1.2 Quality standards for surface water – Heavy Metals

Some additional treatment steps after conventional secondary treatment are required in order to meet more stringent discharge and reuse parameters for both «surface water» and land based effluent dispersal and for indirect reuse applications (Metcalf & Eddy *et al*., 2003).

With the increasing demands for environmental quality standards for "surface water" discharge and reuse, the countries in Europe are constantly improving and finding new technologies to deal with specific inorganic constituents such as heavy metals, that are very toxic to human beings and other organisms (Table 1).

Table 1. Maximum contaminant level of heavy metals in surface water and their toxicities to humans

Heavy metal	Toxicities	Maximum effluent discharge standard (mg/L) (EPA, 2004)
Cd (II)	Kidney damage, renal disorder, Itai-Itai	0,01
Cu (II)	Liver damage, Wilson disease, insomnia	0,25
Ni (II)	Dermatitis, nausea, chronic asthma, coughing	0.20
Zn (II)	Depression, lethargy, neurologic signs such a seizures and ataxia, and increased thirst	1,00

It is perhaps fortuitous that wastewater treatment processes substantially remove most heavy metals, although removal efficiency may vary significantly. Whilst primary sedimentation may be effective in removing insoluble species, removal of soluble species is entirely dependent on the biological stage of wastewater treatment, a phenomena about which comparatively little is known. This aspect can only be understood better through the further development of environmentally applicable speciation methods (Lester et al., 1983).

Dual media filters were installed in the Harnaschpolder WWTP's pilot installation to study the removal of heavy metals such as cadmium (Cd), copper (Cu), nickel (Ni) and zinc (Zn) and to comply with the Dutch norms for water quality (*NW4*). The NW4 (also known as the «*Fourth National Policy Document on Water Management*») is the transposition of the EU's Water Framework Directive into the Dutch legislation. It includes general quality standards for surface water and sediments: the maximum admissible risk with associated maximum permissible concentrations and the negligible risk levels with associated target values (Warmer and van Dokkum, 2002). The calculation of environmental quality standards is a two-stage process:

1. calculation of risk levels (research stage);
2. translation of risk levels into environmental quality standards (policy stage).

Table 1 shows the Maximum Tolerable Risk (MTR) values, according to the *NW4* law for the heavy metals of interest for this research, compared with the average concentrations measured (monthly average) at Harnaschpolder (HNP) WWTP effluent.

Table 2. Maximum permissible risk (MTR) compared with average quality of the HNP's WWTP

Heavy Metals	Concentration Unit	MTR (dissolved)	Harnaschpolder's WWTP average (dissolved)
Cd	µg/L	0,4	<0,3
Cu	µg/L	1,5	<2
Ni	µg/L	5,1	18
Zn	µg/L	9,4	<18

From the table above, it can be observed that the concentrations in the HNP effluent indicate the need for further improvement for removal of heavy metals. At present, the use of filtration technologies (sand filters, dual media filters, etc.) and membranes are being researched for their adequacy for producing surface water and irrigation water from the HNP effluent. Thus far, no studies are being conducted to elucidate the mechanisms and achievable efficiencies of dual media filtration in removing heavy metals, and the influence of related process variables. Therefore it was decided to investigate the removal of heavy metals in a dual media filter inoculated with bacteria tolerant to heavy metals, which might influence the adsorption of such compounds in the filter. The removal of HM using selected bacteria was carried out in a earlier stage (and in a parallel research project) and showed no effective results. Thus,

this research focuses mainly on the physicochemical removal (instead of biological) on four heavy metals, which occur often in high levels in the environment. These metals are: cadmium (Cd), copper (Cu), nickel (Ni) and zinc (Zn).

1.3 The Harnaschpolder WWTP

In the Harnaschpolder region, in Midden-Delfland, bordering on Rijswijk and Delft, one of the largest Wastewater Treatment Plants (WWTP) in Europe was constructed. The development of a classical and environmentally-friendly plant has a maximum capacity of 35,800 m^3/h which allows the need of 1.3 million inhabitants to be met.

This WWTP is composed of several stages of treatment, including a bulky waste removal after the arrival at the treatment plant, a pre-sedimentation tank, an active sludge tank (biological treatment), a post-sedimentation tank and sludge treatment as shown below (Figure 1).

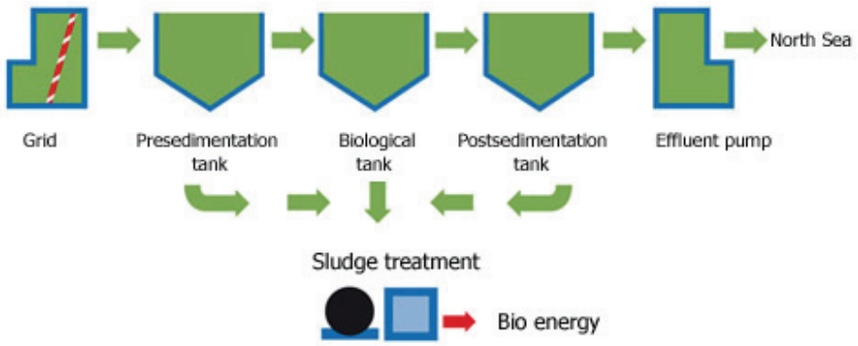

Figure 1. Treatment stages of the Harnaschpolder WWTP

Most of the treated water goes through an underwater emissary to be ejected directly into the North Sea. About 50 m^3/h of the final effluent goes to a research reclamation pilot, which consists of three research lines in operation: a reference line, an innovative line and the pilot line. The reference line consists of a combination of conventional technologies, continuous sand filter, multi media sand filter, UF and RO, whilst the innovation line combines new technologies such as: static bed bioreactor (SBBR), «*biopROtector*» (biological treatment process which makes use of a specific filter medium), flexible fiber filter module (3FM), vertical reverse osmosis in effluent treatment as shown in Figure 2. Both of these treatment lines were built to produce water for multiple end uses such as greenhouse irrigation and surface water. The third and last line (the «*onderzoekslijn*» or «*line of research*») represents the location this project.

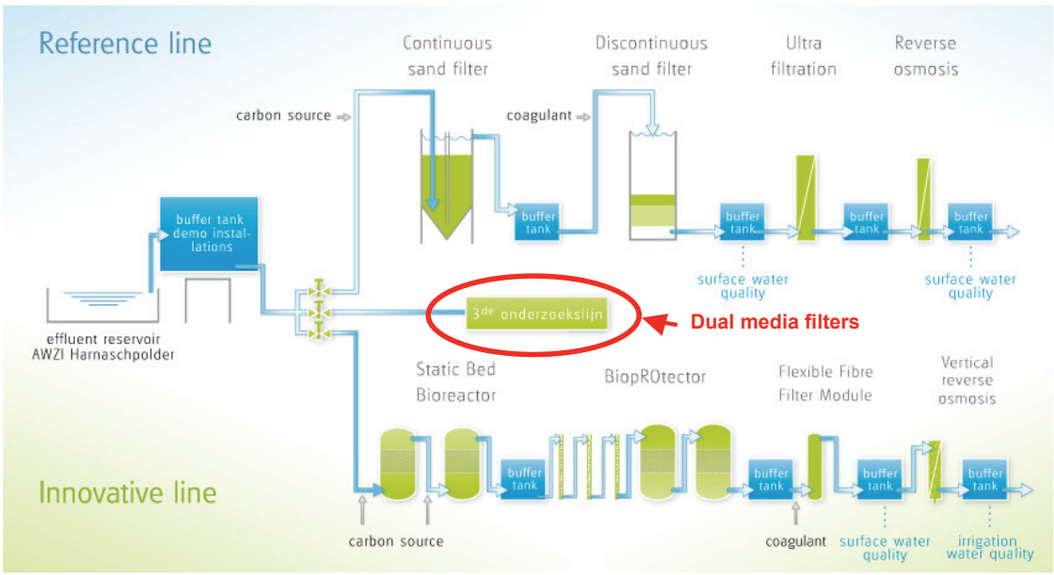

Figure 2. Schematics of the Water Reclamation Pilot in the Harnaschpolder WWTP

1.4 Harnaschpolder's (treated) wastewater parameters

Before the beginning of the filter experiments, an analysis of the Harnaschpolder's WWTP wastewater was carried out. Samples were taken every week (using an automatic water sampler) and its components were analyzed (BOD, COD, DO, nitrates, carbonates, phosphates, sulphites, heavy metals, alkalinity, turbidity, solids, etc.). The following table (Table 3) represents the annual average of the parameters:

Table 3. Harnaschpolder final effluent parameters

Parameter	unit	Avg	Min.	Max.	Number of measurements
EC	µS/cm	989	714	1180	4/49
TSS	mg/l	7,38	0	110	301
TKN	mg/l	2,13	1	8,8	301
NH4-N	mg N/l	0,58	0	3,81	206
BOD5	mg O2/l	3,28	1,4	24	301
COD	mg O2/l	36,89	22	120	301
NO3-N	mg N/l	4,7	0	11	206
PO4-P	mg/l	0,49	0,11	3,06	206
total P	mg/l	0,8	0,12	6,2	301
total N	mg/l	6,83	1,86	13,3	301
Pb	µg/l	2,48	0	7	20
Zn	µg/l	23,75	8	44	20

Parameter	unit	Avg	Min.	Max.	Number of measurements
Cr	µg/l	1,21	0	13	20
As	µg/l	1,23	0	5,4	20
Cu	µg/l	0,83	0	10	20
Cd	µg/l	0,05	0	0,9	20
Hg	µg/l	0,03	0	0,3	20
Cl-	mg/l	133,7	91	170	10
Ca	mg/l	63,6	42	80,9	8
SO4	mg/l	62,5	48	72	4
Na	mg/l	96,9	88,8	105	4
Mg	mg/l	8,56	6,3	10,2	8
K	mg/l	23	20,9	25,1	4
Hardness	mmol/l	2,12	1,48	2,36	8

In the following table (Table 4), there are the quality demands (according to the Dutch quality standards) for greenhouse-type waters.

Table 4. Greenhouse water quality demands

Class 1	unit	value
EGV	µS/cm	<500
Ptot	mg P/l	<15
N-NO3-	mg N/l	<100
N-NH4	mg N/l	<10
SO42-	mg/l	<15
K	mg/l	<200
Ca	mg/l	<80
Mg	mg/l	<12
Fe	µg/l	<50
Mn	µg/l	<200
Zn	µg/l	<150
B	µg/l	<100
Cu	µg/l	<50
Al	µg/l	<10
Cr	µg/l	<5
Pb	µg/l	<1
F	µg/l	<100

Class 2	unit	value
EGV	µS/cm	<500
Ptot	mg P/l	<40
N-NO3-	mg N/l	<150
N-NH4	mg N/l	<10
SO42-	mg/l	<40
K	mg/l	<350
Ca	mg/l	<150
Mg	mg/l	<40
Fe	µg/l	<500
Mn	µg/l	<500
Zn	µg/l	<450
B	µg/l	<200
Cu	µg/l	<150
Al	µg/l	<20
Cr	µg/l	<5
Pb	µg/l	<1
F	µg/l	<100

2. OBJECTIVES OF THE RESEARCH

The objectives of this research are:

- To make a review on the different mechanisms for the removal of heavy metals from treated urban wastewater;
- Simulate solubility curves for the following heavy metals: Cd, Cu, Ni and Zn in wastewater with a physicochemical composition similar to the HNP treated effluent (heavy metals, alkalinity, pH, temperature, redox, nitrates and other ions, etc), using the PHREEQc computer simulation software;
- Based on the lab-scale results and the PHREEQc simulation, suggest possible physicochemical removal mechanisms for heavy metals, from the Harnaschpolder WWTP effluent.
- Also, based on the experimental data (both filter experiments and simulation), estimate the percentage of HM removal by physic-chemical processes in order to assess the performance of the bacteria-inoculated filters in the parallel research.

3. OVERVIEW OF THE RESEARCH

Stage	Observations
1. Dimensioning & assembly of the filters at the HNP's WWTP Pilot Installation.	Assembling the filters the best possible way, to prevent future leaks and/or other operational hazards. An operation and safety manuals were written in parallel to this practical stage.
2. Start-up	Testing the system for possible leaks; adjust backwash system (air and fresh water); adjust feeding system (keeping the influent flow steady).
3. First run («*Blank run*»)	Running the filters without addition being of heavy metals or carbon required for denitrification. Parameters such as turbidity, head loss, COD and NO_3 – were analyzed.
4. Heavy metal dosing	Heavy metals such as Cd, Cu, Ni and Zn, were added to the filters with a concentration of 250µg/L. Parameters such as turbidity, head loss, COD and NO_3 – and heavy metals were analyzed.
5. PHREEQc simulation	Based on the physicochemical conditions present in the filters, solubility curves were simulated for the heavy metals studied in this research.
6. Results comparison	Results from the experimental data (% of HM removal) and PHREEQc simutation (solubility curves) were compared

4. LITERATURE REVIEW

4.1 Heavy metal removal processes

Facing with more and more strict regulations, heavy metal pollution is gradually becoming one of the most serious environmental problems. Therefore, toxic heavy metals should be removed from the wastewater to protect both people and environment (Singh *et al*., 2004). Many methods can be used to remove heavy metal ions, which include chemical precipitation, ion-exchange, biosorption, adsorption, membrane filtration, electrochemical treatment technologies, etc. Although there are a great variety of treatments available, they have their inherent advantages and limitations in their application (Table 5).

Table 5. Summary of the different possibilities of physicochemical removal for wastewater

Type of treatment	Target of removal	Advantages	Disadvantages	References
Chemical precipitation	HM, divalent metals	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal	(Wang *et al*., 2006)
Coagulation--flocculation	HM and suspended solids	Shorter time to settle out suspended solids, improved sludge settling	Sludge production, extra operational cost for sludge disposal	(Shammas, 2005)
Dissolved air flotation	HM and suspended solids	Low cost, short hydraulic retention time	Subsequent treatments are required to improve the removal efficiency of HM	(Lazaridis *et al*., 2001)
Ion Exchange	Dissolved components, cations/anions	No sludge generation, less time consuming	Not all ion exchange resins are suitable for HM removal, high capital cost	(Rengaraj *et al*., 2003)
Ultrafiltration	High molecular weight compounds	Smaller space required	High operational cost, prone to membrane fouling	(Vigneswaran *et al*., 2005)
Nanofiltration	Sulphate salts and hardness ions	Lower pressure than RO	High energy consumption due to high pressures	(Ahn *et al*., 1999)
Reverse Osmosis	Organic and inorganic compounds	High rejection rate, able to withstand high	High pressure required, membrane fouling	(Vigneswaran *et al*., 2005)

– Dual media filtration

Miska (2009) investigated the extent of both biological and physicochemical uptake of heavy metals, through denitrifying biomass contributing to the heavy metal removal in a pilot scale project on the WWTP Horstermeer, in the Netherlands.

In the author's experiments, primary Jar-tests were conducted to test the ability to remove the so-called «conventional» parameters and simultaneously removing heavy metals. For this experiments, standards solutions of HM were also made (Nickel: 1000mg/L, Zinc: 100mg/L, Copper: 100mg/L) to dose in the pilot's effluent. The removal efficiencies for the HM were compared by subjecting to three different coagulants: poly aluminium chloride, ferric chloride and powdered activated carbon in order to promote co-precipation.

The results of HM removal with co-precipitation with aluminium showed a relatively high removal of copper (79%) and an extremely low removal for nickel (15%). The efficiency removal for zinc and copper were 38% and 20% respectively, when using ferric chloride as coagulant. The dosage of powdered activated carbon resulted in a removal efficiency of 95% for both zinc and nickel (Miska-Markusch, 2009).

The filter experiments were realized at Horstermeer Pilot installation at the WWTP in the Netherlands. The pilot installation consisted of two dual media filters (upper layer: anthracite, 80cm height; lower layer: quartz sand, 40cm height), assembled to work in parallel (one of them used as a control). The flow rate in operation was set to $8m^3/h$ (filtration rate 10m/h), resulting in filtration run times between 4h (initial stage) and 24h (in a final stage).

In the experiments, a heavy metal solution containing copper, nickel and zinc was prepared from metal chlorides and dosed to maintain a concentration of 120-150µg/L of each metal in the filters treating WWTP's effluent.

Final concentrations of HM were measured in both filters through cuvette analyses. Methanol and coagulant were also dosed as a carbon source for denitrification (of the pre-existent bacteria in the wastewater) and chemical precipitation of phosphorus, respectively.

These experiments were then subjected to different conditions such as the dosing of methanol, dosing of coagulant and the duration of the experiments.

As a result, the removal efficiency of the fraction of the total inorganic copper (particulate form) reached as high as 92% when the filters were dosed with coagulant and methanol. The copper dissolved fraction was extremely low (25mg/L), compared to the other metals.

The measurements for nickel present remarkably different results for copper: the dual media filter did not retain the dissolved form and the highest removal efficiency was only 25% when subjected only to carbon dosing.

The major concentration of zinc is in dissolved form, the same as nickel, but is partly removed in the dual media filter with approximately 60% of efficiency (Miska-Markusch, 2009).

4.2 Heavy metal removal mechanisms

In recent years, different treatment mechanisms have been studied for removal of heavy metals in wastewater to improve the quality of the treated effluent. Such mechanisms include chemical precipitation, biosorption, micro-precipitation, adsorption and others.

Chemical Precipitation

Chemical precipitation in water and wastewater treatment is the change in form of materials dissolved in water into solid particles. It is widely used for heavy metal removal from industrial effluents because its relatively simple and inexpensive to operate (Ku and Jung, 2001). The forming precipitates can be separated from the water by sedimentation or filtration so that the final effluent can be appropriately discharged or reused (Fu and Wang, 2011).

Most metals are precipitated as hydroxides, but other methods such as sulfide and carbonate precipitation are also used. In some cases, the chemical species to be removed must be oxidized or reduced to a valence that can then be precipitated directly.

The chemical equilibrium relationship in precipitation that affects the solubility of the component(s) can be achieved by a variety of means. One or a combination of the following processes induces the precipitation reactions in a water environment (Wang *et al*., 2006).

Despite having operational and economic advantages, i.e. it is very simple to introduce the chemical into the wastewater and it is very cheap to do so, there are some disadvantages to take into consideration. Firstly, this process generates toxic sludges that need special attention to dispose (e.g. these chemical sludges must be disposed in special landfills or incinerators). Thus, it will add an extra cost to the operation of the WWTP. This also applies for other chemical precipitation processes such as coagulation/flocculation.

– Hydroxide precipitation

Hydroxide precipitation is the most widely used chemical precipitation technique, due to its relative simplicity, low cost and ease of pH control (Huisman *et al*., 2006). The solubilities of the various metal hydroxides are minimized in the pH range of 8.0-11.0 for posterior removal by flocculation, sedimentation or filtration processes. A variety of hydroxides has been used to precipitate metals from wastewater, based on the low cost and ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings (Baltpurvins *et al*., 1997) (Table 6).

Table 6. Heavy metals removal by using chemical precipitation (Fu and Wang, 2011)

Species	Initial conc.	Precipitant	Optimal pH	% Removal
Zn^{2+}	32 mg/L	CaO	9.0-10.0	99
Cu^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}	100 mg/L	CaO	7.0-11.0	99
Cu^{2+}, Zn^{2+}, Pb^{2+}	0.018, 1.34, 2.3 mM	H_2S	3.0	100, >94 , >92
Cr^{3+}	5363 mg/L	CaO, MgO	8.0	>99
Hg^{2+}	65.6, 188 µ/L	1,3-benzenediamidoethaneth iolate	4.7-6.4	>99

Mirbagheri *et al.* (2005) studied the removal of hexavalent chromium from wastewater using calcium and sodium hydroxides. Results of their experiments showed that the maximum precipitation was obtained at a pH of 8.7 and the concentration of chromate was reduced from 30 mg/L to 0.01 mg/L (99% efficiency). Copper removal was also tested in the same experiments and the optimum pH for maximum precipitation was about 12, obtaining an efficiency of 98.5% (Mirbagheri and Hosseini, 2005).

In hydroxide precipitation process, the addition of coagulants such as alum, iron salts, and organic polymers can enhance the removal of heavy metals from wastewater.

Although widely used, hydroxide precipitation also has some limitations. Firstly, hydroxide precipitation generates large volumes of relatively low density sludge, which can present dewatering and disposal problems (Kongsricharoern and Polprasert, 1995). Secondly, some metal hydroxides are amphoteric, i.e. react as an acid as well as a base, and the mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may put another metal back into solution.

Thirdly, when complexing agents are in the wastewater, they will inhibit metal hydroxide precipitation.

– Sulfite precipitation

Sulfide precipitation is also an effective process for the treatment of heavy metals ions. Both «soluble» sulfides such as hydrogen sulfide or sodium sulfide and «insoluble» sulfides such as ferrous sulfide may be used to precipitate heavy metal ions as insoluble metal sulfides (Wang *et al*., 2006). The main advantage of using sulfides is that the solubilities of the metal sulfide precipitates are dramatically lower than hydroxide precipitates and sulfide precipitates are not amphoteric. This translates in a higher degree of metal removal over a broad pH range when compared with hydroxide precipitation. Also, the sludges formed in sulfite precipitation exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges.

Kousi *et al.* (2007) developed a new precipitation process based on sulfate-reducing bacteria (SRB), which consisted in oxidizing simple organic compounds, under anaerobic conditions, and transforming them into hydrogen sulfide. The hydrogen sulfide then reacts with divalent soluble metals to form insoluble metal sulfides, according to the following equation:

$$M^{2+}_{(aq)} + H_2S_{(g)} \rightarrow MS_{(s)} \downarrow + 2H^{+}_{(g)}$$

According to the authors' experiments, who developed an upflow fixed-bed SRB filter to monitor for the treatment of zinc-bearing wastewater, it was proved that this type of reactor has a considerable capacity of completely reducing sulfates with a maximum removal efficiency of 93% of zinc (Kousi *et al*., 2007).

Despite the obvious advantages, there are also potential dangers in the use of sulfide precipitation process regarding the release of toxic H_2S fumes, when the HM ions are subjected to acid conditions. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes.

The following graph (Figure 3) shows the solubility curves for both hydroxides and sulfides and their variation according to the pH.

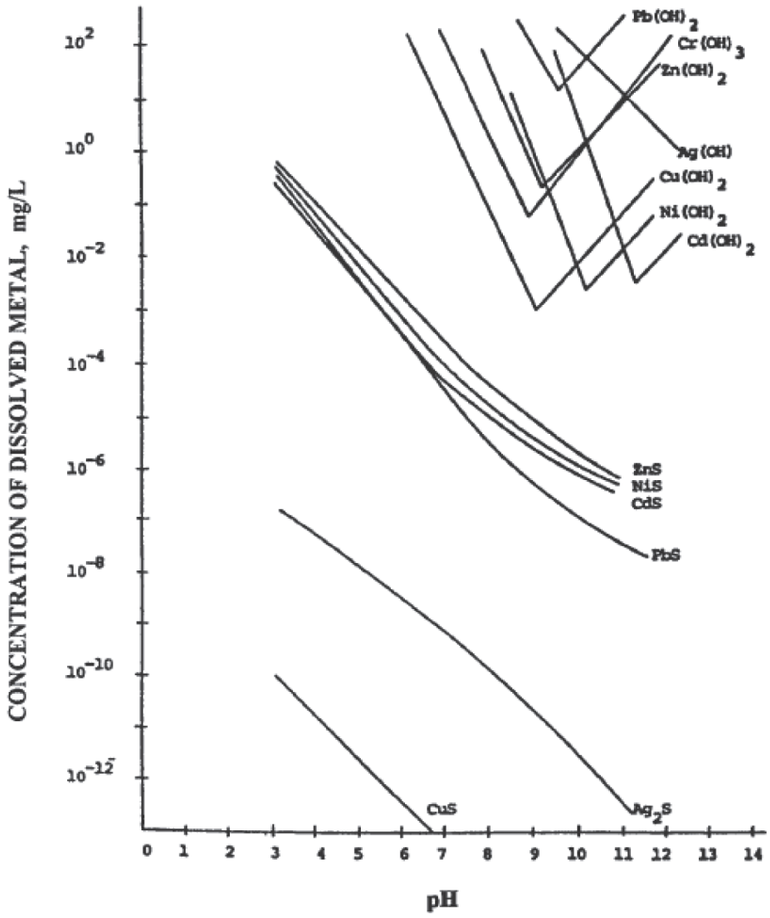

Figure 3. Solubility of hydroxides and sulfides as a function of pH (Wang *et al*., 2006)

In the graph above, it is clear that metal sulfides have lower solubilities than hydroxides, in the alkaline pH range, and also tend to have low solubilities at or below the neutral pH value. This means that in higher pH values, heavy metals precipitate mostly in the form of hydroxides rather than sulfides.

– Carbonate precipitation

Carbonate precipitation may also be used to remove metals either by direct precipitation using a carbonate reagent such as calcium carbonate or using carbon dioxide. The solubility of most metal carbonates is intermediate between hydroxide and sulfide solubility; in addition, carbonates form easily filtered precipitates. There are other processes such as cyanide precipitation and co-precipitation that can be used to remove heavy metals (Wang *et al*., 2006) (EPA, 2000).

– Cyanide precipitation

Cyanide precipitation, although a method for treating cyanide in wastewater, does not destroy the cyanide molecule, which is retained in the sludge that is formed. Reports indicate that during exposure to sunlight, the cyanide complexes can break down and form free cyanide. For this reason the sludge from this treatment method must be disposed of carefully. Cyanide may be precipitated and settled out of wastewater by the addition of zinc sulfate or ferrous sulfate, which forms zinc ferrocyanide or ferro – and ferri-cyanide complexes. In the presence of iron, cyanide will form extremely stable cyanide complexes (Wang *et al.*, 2006, Botz *et al*., 2005).

– Heavy metal chelating precipitation

This occurs when organic molecules, containing more than one functional group with donor electron pairs, can simultaneously donate these to a metal atom, forming a ring structure. In general, since a chelating agent may bond to a metal ion in more than one place simultaneously, chelated compounds are more stable than complexes involving monodentate ligands. Stability tends to increase with the number of chelating sites available on the ligand. Thus chelation of metals by donor ligands of biopolymers leads to the formation of stable species (Tsezos, 2007). The use of this mechanism in wastewater treatment is an economically viable alternative since commercial heavy metal precipitants today either lack the necessary binding sites or pose too many environmental risks to be safely utilized, compared to synthesized chelating agents (Matlock *et al*., 2002).

– Bio-precipitation

The selective sequestering of metal soluble species that result in the immobilization of the metals by microbial cells is also known biosorption (Tsezos, 2007). It results on the binding of metals and metalloid species, compounds and particulates from solutions to functional groups on the cell surface polymers (Diels *et al*., 2003) (Wang and Chen, 2009).

Biosorption is a process with some unique characteristics. It can effectively sequester dissolved metals from very dilute complex solutions with high efficiency. This makes biosorption an ideal candidate for the treatment of high volume low concentration complex wastewaters (Tsezos, 2007). The mechanisms that occur in biosorption mechanisms are similar to the physicochemical mechanisms which include: complexation, where metal ions are binded with organic molecules, involving the ligand centres in the organic species (Avery and Tobin, 1993) and micro-precipitation, where the precipitates may be formed and remain in contact with or inside the microbial cells or may be independent of the solid phase of the microbial cell (Remoudaki *et al*., 2003).

The biomass generated in this process generates alkalinity, which alters the chemical microenvironment of the biofilm, by increasing the pH and carbonate concentration of the growth medium and

could lead to a chemical precipitation of heavy metals as hydroxides (Remoudaki *et al*., 2003, Hussein *et al*., 2005).

– Chemical Adsorption

Adsorption has been successfully applied for treating municipal and drinking water. Successful removal of heavy metals from aqueous solutions using, for example, activated carbon has recently been demonstrated (Barakat, 2011, Bansal *et al*., 1988). Chemical adsorption is considered one of the best available technologies for eliminating non-biodegradable and toxic organic compounds from aqueous solutions, such as heavy metals (Benjamin *et al*., 1982). Its inherent physical properties such as a large surface area (500-2000 m^2/g), porous structure, high adsorption capacity and extensively reactive surface, make it extremely versatile (Barakat, 2011).

Solids with oxide surfaces can act as weak acids and bases in solution. The surface ions function as ion exchange sites. While increasing the pH, the adsorption of cations increases and adsorption of anions decreases. The adsorption capacity will change from 0% to 100% of the adsorbent's total capacity over a narrow range of one or two pH units. (Leyva Ramos *et al*., 2002).

Complexing agents can either increase or decrease adsorption. They may decrease adsorption by stabilizing the ion in solution.

Alternatively, they may increase it by forming complexes that adsorb stronger than the ion alone. For example, cyanide can strongly increase adsorption of nickel ions at high pH values (Petrov *et al*., 1992, Marzal *et al*., 1996).

– Denitrification and heavy metals removal

Secondary effluents from wastewater treatment plants still contains several microorganism including heterotrophic organism, which are able to denitrify and remove nitrate nitrogen NO_3-N, when an electron donor is present.

Biological denitrification involves the biological oxidation of many organic substrates in wastewater treatment using nitrate as the electron acceptor instead of oxygen. In biological nitrate reduction process, the electron donor is typically one of the three sources:

(1) the COD in the influent wastewater;
(2) the COD produced during endogenous decay;
(3) an exogenous source such as methanol or acetate (Metcalf & Eddy *et al*., 2003).

Alkalinity is produced in denitrification reactions and the pH is generally elevated (Metcalf & Eddy *et al*., 2003). Davis *et al*., (2007) reported that acidic conditions lead to dissolution of precipitated Zn and Cu and increase their mobility in a filter column set-up. Furthermore, the impact of redox altering compounds on the fate of Zn, Cd and As with and without carbon source (acetate) was investigated

through batch experiments. As a result, it was revealed that in the presence of both nitrate and sulphate, denitrification was the dominant process affecting metal behavior (Davis *et al.*, 2007, Vanbroekhoven *et al.*, 2007). In addition, the removal of Cd and Zn in the presence of an electron acceptor (nitrate) with and without carbon source (acetate) was tested in column experiments, consequently it was concluded that the metals removal efficiency went up to close to 100% for both cases, however the mechanism of removal were different.

4.3 PHREEQc Software Simulation

PHREEQC is a software for simulating chemical reactions and transport processes in natural or polluted water. The program is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces, but also includes the capability to model kinetic reactions with rate equations that are completely user-specified in the form of Basic statements. Kinetic and equilibrium reactants can be interconnected, *e.g.* by linking the number of surface sites to the amount of a kinetic reactant that is consumed (or produced) during the course of a model period.

PHREEQC is based on the Fortran program PHREEQE (Parkhurst *et al.*, 1990), capable of simulating a variety of geochemical reactions for a system including:

- Mixing of waters;
- Addition of net irreversible reactions to solution;
- Dissolving and precipitating phases to achieve equilibrium with the aqueous phase;
- Effects of changing temperature, ion-exchange equilibrium, advective transport, surface--complexation equilibrium and much more.

The numerical method has been modified to use several sets of convergence parameters in an attempt to avoid convergence problems. User-defined quantities can be written to the primary output file and (or) to a file suitable for importation into a spreadsheet, and solution compositions can be defined in a format that is more compatible with spreadsheet programs.

– Software potential in water and wastewater treatment

PHREEQc is generally used for water chemistry in geo-hydrology but hardly applied in water treatment, mainly because of the absence of scientific literature/educational material on water treatment with PHREEQc (Moel *et al.*, 2011).

However this software can be extremely useful for water and wastewater treatment because it can simulate and «predict» the various possible interactions that occur in aqueous solutions, *e.g.* precipitations, complexations, ion-exchange equilibriums/reactions, given a certain water composition.

- **Batch-Reaction Modeling** – applied to problems in laboratory, natural, and contaminated systems. The reaction capabilities of PHREEQc have been used frequently in the study of mine drainage, radioactive decay, etc.
- **Speciation Modeling** – useful in situations where the possibility of mineral dissolution or precipitation needs to be known, as in water treatment, aquifer storage and recovery, artificial recharge, and well injection. It uses the chemical analysis of a water to calculate the distribution of aqueous species by using an ion-association aqueous model (Zhang *et al.*, 2011). The results of speciation calculations are saturation indexes for minerals, which indicate whether a mineral should dissolve or precipitate (Charlton and Parkhurst, 2011).

To make all the calculations, the program uses various databases. The database file includes all the thermodynamic data used to make the saturation calculations and parameters for estimating the activity coefficients.

The «default» database of PHREEQc is «*Phreeqc.dat*», used for general purposes. The recommended database for water treatment is «*Wateq4f.dat*» (Moel *et al.*, 2011), which result on the continuous compilation of information from literature and experimental data.

In this work, PHREEQc was used to calculate saturation indexes and distribution of the heavy metals in the filter medium (treated wastewater from the HNP WWTP and heavy metal dosing). The saturation indexes will then determine if the heavy metals will precipitate or stay dissolved in the solution, depending on the filters conditions (pH, temperature, alkalinity/acidity, redox, nitrates, sulfates, presence of other ions).

– Simulation of metal solubility as a function of pH from sludge samples

Using PHREEQc software, Remoudaki *et. al* (2003) simulated solubility curves of Nickel, Zinc and Copper, which indicate dominant insoluble species for the metals of interest (using «*wateq4f.dat*» as the main database), to make a comparison between the experimental data from bio-sorption sludges (containing high doses of HM) and the solubility curves at different pH values (with the same conditions as the experimental data). This helped to understand the mechanisms involved inside the filter medium.

In his experiments, the three heavy metals were selected taking into account the anions present in the sampled wastewater that can form insoluble species with the metal ions (cations) in the filter environment.

As a result, the curves presented the concentration of certain metal in solution at equilibrium with the solid phase (saturation index < 0), showing that metal-carbonate species were the most soluble among other compounds like metal-hydroxides, metal-phosphates and metal-sufiltes (Figure 4 to Figure 6). In contrast, the most insoluble compounds were the metal sulfide precipitates leading to the lowest equilibrium soluble metal concentrations due to the fact that the reactions occurred under anoxic sulfate reducing conditions which offers a superior advantage for metal ion precipitation (Remoudaki *et al*., 2003).

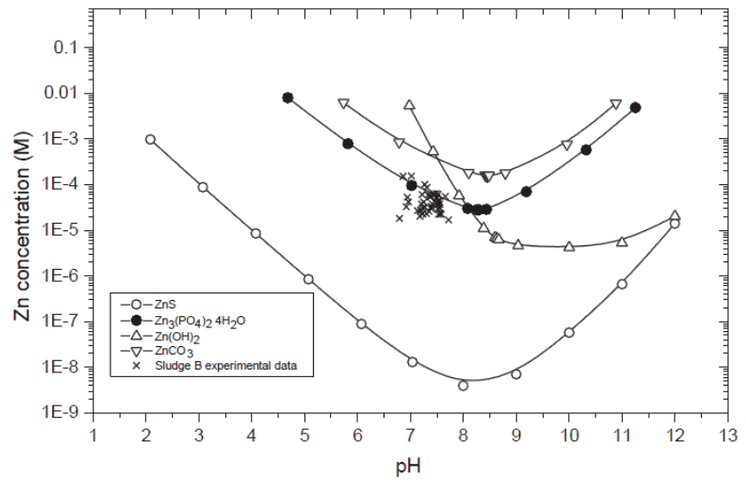

Figure 4. Zinc solubility diagram as function of pH

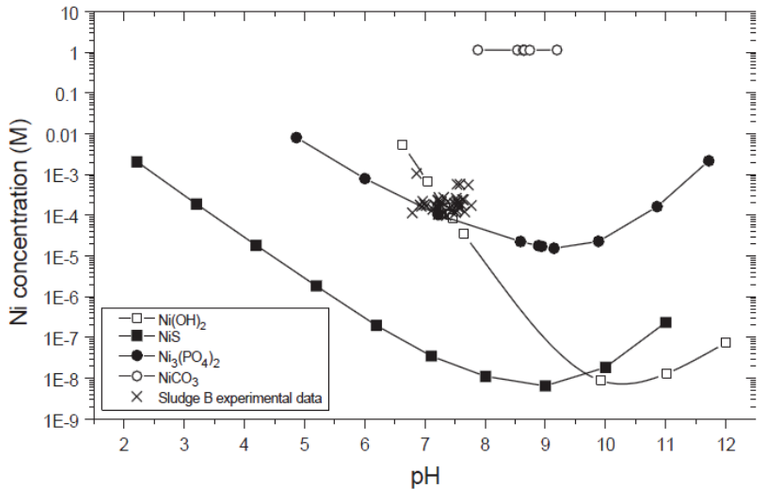

Figure 5. Nickel solubility diagram as function of pH

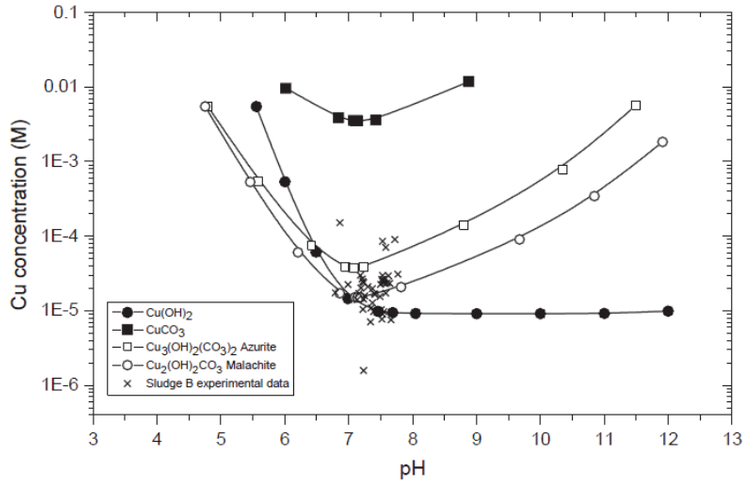

Figure 6. Copper solubility diagram as function of pH

From the figures above, it is observed that the most soluble species are metal-carbonates ($M\text{-}CO_3$) since they have the highest equilibrium soluble concentrations in all three metals (copper, nickel and zinc). Metal phosphates are also very soluble comparing to the remaining phases.

Moreover, from these figures is observed that the most insoluble compounds are the metal sulfide precipitates leading to the lowest equilibrium soluble metal concentrations. It is expected that the operation of processes under anoxic sulfate reducing conditions offers a superior advantage for metal ion precipitation (Clarke *et al.*, 1997, Van Hille *et al.*, 1999).

5. MATERIALS AND METHODS

5.1 PHREEQc Simulation

As referenced before, PHREEQc has a large potential for application in water treatment. In its basic form all relevant chemical equilibriums for water chemistry are incorporated, including all redox reactions.

For this simulation, the «user friendly» of PHREEQc software was used (*version 2.18.3-5570* from the US Geological Survey), also called «*PHREEQc Interactive*».

– Development of the input file

PHREEQc software uses the keyword «*SOLUTION*» and «*SOLUTION_SPREAD*» for input of elements in the solution. It uses chemical elements, such as Ca, H, O, Na, and C as prime input parameters. These elements might be subdivided into redox states of an element, such as C(+4) and C(-4) or Fe(+2) and Fe(+3). The elements and their definitions are relatively easy to insert into the program and they are given by different databases that comes with the software (Figure 7).

PHREEQc uses the «*mole*» as the default quantity for elements and «*kg*» (or *kgw* – quilograms of water) as the default quantity for the solvent. The amount of substance for an element in solution is calculated from its molal concentration (molality in mol/kgw) and the mass of water (by default 1 kg).

The elements H and O have a special status in PHREEQc because of their multiple appearances (H_2O, H^+, OH^-, O_2, H_2) in the solution, and H_2O being the solvent in PHREEQc.

In PHREEQc the speciation of elements is calculated from the pH and *pe* value (activity of each specie). The activity is a measure of the «effective concentration» of a species in a mixture, meaning that the species' chemical potential depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution.

The *pe* value is calculated from the redox couple (in the database) if it is not directly specified in the input file.

The keyword END marks the end of the input, and starts the calculation of the simulation. The final results (the output file) can be automatically exported to a spreadsheet (MS Excel) in order to make a graphical representation of the results (Parkhurst, 1999).

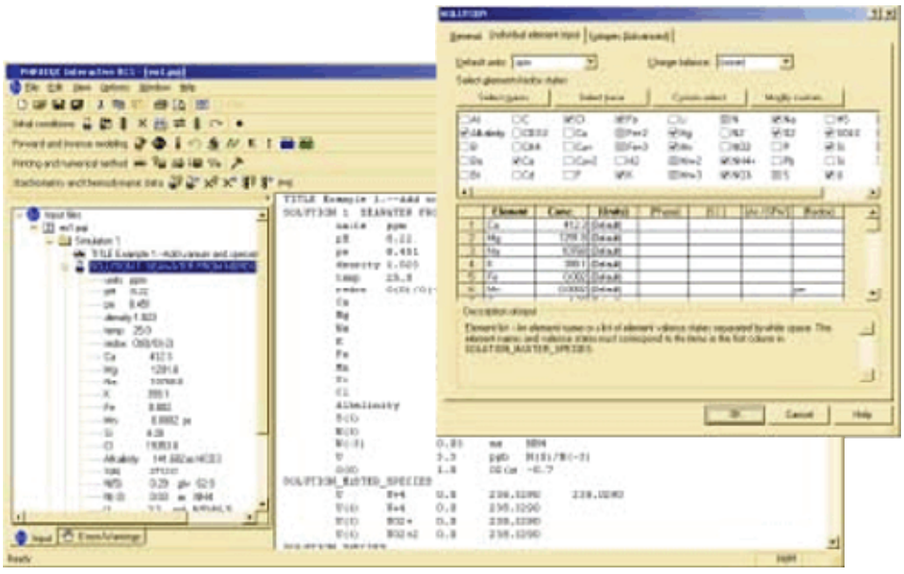

Figure 7. Main screen of PHREEQC, with the SOLUTION keyword dialog box open.

– Writing the input file

In order to simulate a reaction between the influent (treated wastewater, containing traces of HM's and other substances) and the HM mother solution (concentrated solution of heavy metals that is pumped into the filter), the input file was separated in five different steps:

SOLUTION 1 – Filter's influent (HNP's WWTP treated wastewater)

SOLUTION 2 – Heavy metals solution (containing heavy metal chlorides' solution)

SOLUTION 3 – Fictitious solution that results in the mix of the previous solutions

EQUILIBRIUM PHASES – Simulates the equilibrium phase of each form of heavy metal, *i.e.* verifies if any available form of heavy metal forms a precipitate.

REACTION – Addition of a base (NaOH) to simulate the variation of the heavy metals precipitates solubility, according to the pH. Sodium hydroxide was (virtually) added instead of an acid, because the effluent was slightly acidic.

Firstly, the average values of Harnaschpolder's WWTP effluent were inserted into «SOLUTION 1» (Table 7).

The database was set to «*llnl.dat*» (instead of «*wateq4f.dat*» used in Remoudaki's experiments) because it is the most complete database regarding the information about all known inorganic aqueous species and minerals, especially heavy metals.

After setting the working database for the modeling, SOLUTION 2 (containing a single heavy metal) was introduced into the input file.

Table 7. Physicochemical parameters used in SOLUTION 1

Parameter	Value*	Unit
Temperature	19	ºC
pH	6.52	-
COD	35	mg/L
NH_4	0.5	mg/L
NO_3	4.4	mg/L
TSS	2.9	mg/L
Ni (dissolved)	18	µg/L
Zn (dissolved)	<18	µg/L
Cd (dissolved)	0.3	µg/L
Cu (dissolved)	2	µg/L
Pb (dissolved)	8.2	µg/L

* average values of HNP's treated effluent, retrieved from Delfluent website (www.delfluent.nl)

After introducing the initial solutions, both solutions were «virtually» mixed, at a ratio of 0.90/0.10, *i.e*. a fraction of 0.90 is taken from the first solution while a fraction of 0.10 was taken from the second solution, generating another solution (SOLUTION 3). This ratio is very important because the flows are not equal, meaning that the feeding flow (wastewater) is 90% bigger than the heavy metal dosing flow. Finally, the reaction between the sodium hydroxide (strong base) and the resulting solution was introduced into the input file along with the possible precipitate forms of each heavy metal (*e.g.* for Copper: azurite, malachite, $Cu(OH)_2$, etc.). Pressing the «Calculate» button, PHREEQc calculates the concentration of each type of (possible) precipitate, under the operating conditions.

– The output file

The output of PHREEQC is a huge collection of calculated values, which lacks easy access for user specific information. The values in the output have been automatically converted into the units of the experiments.

The output of PHREEQc is usually grouped in 5 different sections, as shown in Table 8. The last part of the output file, the «*Saturation indices*» contain all the information necessary to build the graphs (Moel *et al.*, 2011).

Table 8. PHREEQc output section

Output section	Description	Main purpose
Solution composition	Molality and moles for all elements[3]	Input check
Description of solution	General parameters[4]	Calculated overall parameters
Redox couples[1]	*pe* and *redox* potential for all redox couples	Electron balance in input
Distribution of species	Molality, activity and gamma of all species, with total molality per redox state of an element[5]	Speciation
Distribution of alkalinity[2]	Contribution in alkalinity per dissolved specie, with molality and	Acid-base buffering
Saturation indices	SI, IAP and K values for all phases	Relation to gas and solid phases

1 Only in initial calculation, when unbalanced redox couples are present
2 Only in output if –alkalinity=true under PRINT
3 For initial calculation: including molality and moles for inputted redox states
4 For initial calculation: including Total CO2, if Alkalinity is in the input
5 For initial calculations: for elements with multiple redox states only the inputted redox states

5.2 Filter operation

Two dual media filters were assembled and started up in the wastewater reuse pilot at Harnaschpolder WWTP. The filters were assembled and started up, for a further evaluation on removal of Cd, Cu, Ni and Zn (carried out through a parallel research).

In a first stage, two identical columns were operated in parallel under the same operational conditions (*i.e.* same feeding flow, outflow, hydraulic retention times, etc.). In a second stage, maintaining the same operational conditions, both filters were dosed with specific concentrations of Cd, Cu, Ni and Zn so that the removal efficiencies of these heavy metals could be compared with solubility curves simulated by PHREEQc. The last two experiments were also subjected to the same operational conditions as the first stage.

During all the stages, an ion exchange system was required to make sure that the effluent of these filters remained clean and metal-free, to meet the discharge guidelines.

Besides the removal of heavy metals, COD, NO_3 – and turbidity as well as the influence of pH were evaluated in a parallel work (Villarroel Toral, 2011).

– Filters set-up

The filters, operated in parallel, consisted of two down flow columns of manual control.

The filters were operated at constant rate (the water level was constant, meaning that the inflow was equal to the outflow) and continuously fed by treated effluent from HNP WWTP. Figure 8 and Figure 9 show the installation of the filters in the Pilot Plant at HNP.

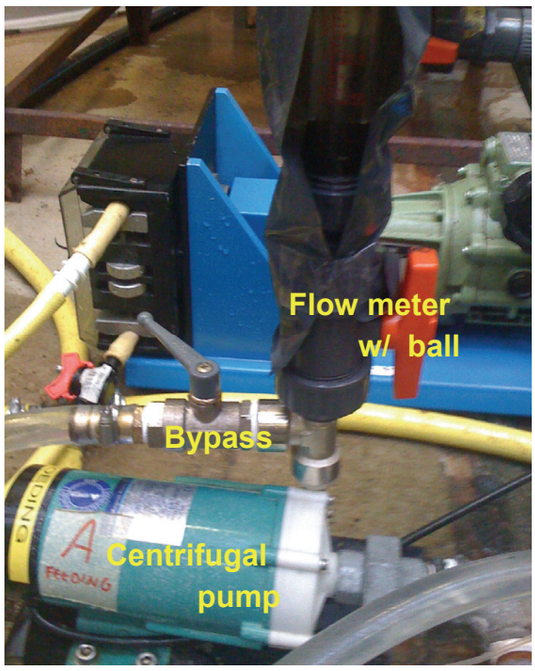

Figure 8. Detail of the feeding system

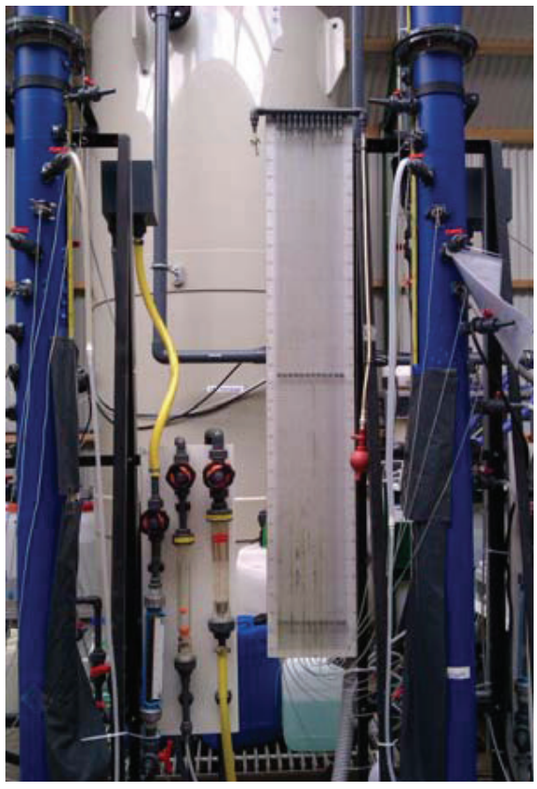

Figure 9. Dual media filters HNP's Pilot Plant

The filter columns, made of transparent acrylic, were 3m high (in total) and had an internal diameter of 13 cm. The filter bed area is 0.013m^2. The effective sand and anthracite bed heights were 105cm and 45cm respectively. The effective height was 2.0m and the filter bed area as shown in Figure 10.

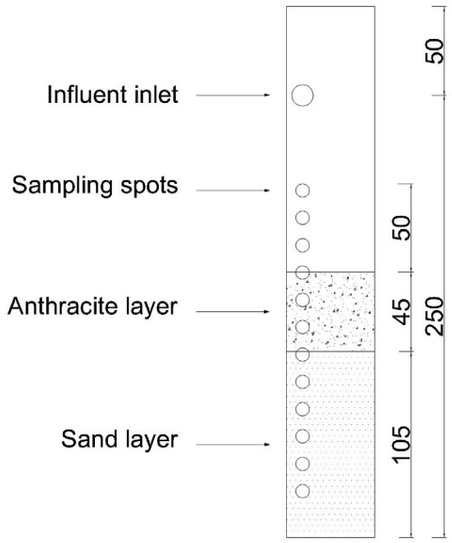

Figure 10. Detail of the filter column (values in cm)

The filter bed was filled with a bottom layer of sand with a diameter between 1.5 – 2.5 mm, with a density of 1600 kg/m^3 and with a top layer of anthracite with grain diameter of 2 – 4 mm and, a density of 700 kg/m^3. The filters, the flow meters and also other translucid or transparent equipment were covered to prevent unwanted biomass growth.

A pressure gauge, a feeding pump (for wastewater), a head loss regulator, a HM dosing system (for individual dosing, also for carbon dosing) connected to peristaltic pumps (Watson-Marlow 200 series) and fresh water and air connections (for backwash) were made for each filter.

In the Figure 8 it is possible to see the different solutions for the feeding system that were tested during the start-up phase:

- Centrifugal pumps: they pump the treated wastewater from the HNP Pilot Buffer Tank (main tank that receives a very small percentage of the WWTP's final/treated effluent) directly to the filters. The flow is then regulated though a ball-valve system.
- By-Pass: since the Pilot Buffer tank was elevated, it had enough pressure to feed the filters without using the (feeding) pumps. Thus, reducing the energy consumption and guarantees a more constant pressure.

The lab scale filters that were installed at the Harnaschpolder's Pilot Plant, were built according to dimensions and operational parameters in Table 9.

Table 9. Dimensions and operational parameters of the lab-scale filters

Dimensions and operational parameters	Value	Unit
Diameter	0.13	m
Filter height	2.00	m
Sand bed height	1.50	m
Sand porosity (Φ)	1.4 – 2	mm
Feeding velocity rate:	5 to 15	m/h
Backwash velocity rate:	15 to 75	m/h
Starting point backwash*:	1.5 min with air, 1 min (air+water), 0.5 min water	

* theoretical times, according to Miska-Markusch (2009)

The filters were initially assembled according to Figure 11, which give a simples description of the setup for an easy understanding of their operation. The filters setup was constantly modified in order to comply with several safety, operational and practical restrictions that were imposed at the HNP's Pilot Plant.

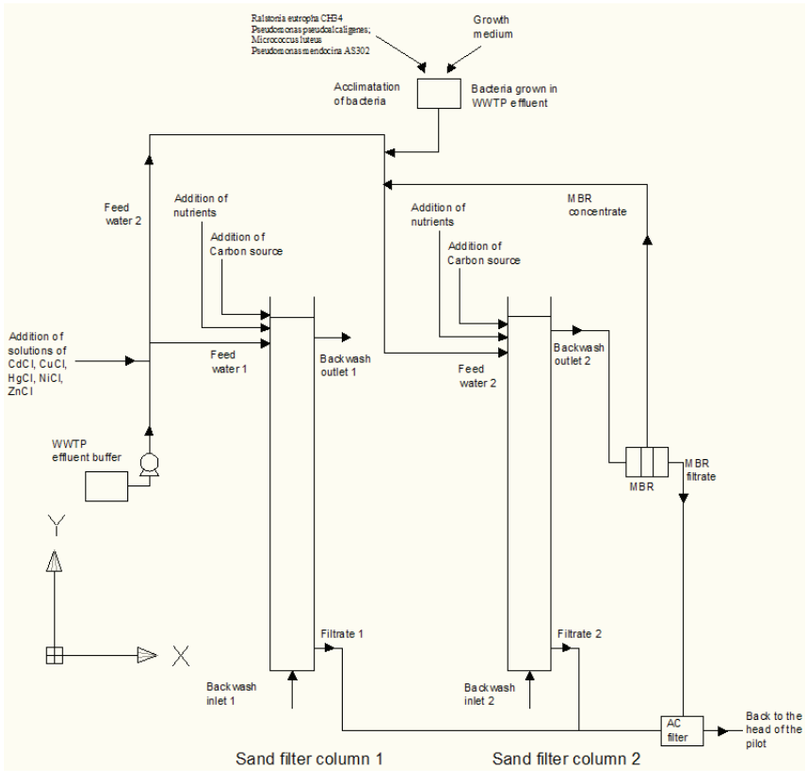

Figure 11. Concept design for filter experiments with selected pure bacteria

Throughout the design process of the lab scale filters, several drawings were made in order to specify the direction and types of flows (wastewater inlets, clean water, compressed air, heavy metals, methanol, effluent, biomass), equipments (pumps, valves, tanks) and other details. These drawings are available in the «Appendix I» section.

The filters were firstly partially assembled at TU Delft's sanitary engineering lab's to make sure everything was water tight. After checking the filters, they were brought to Harnaschpolder's Pilot Plant for the final assembly (Figure 12).

Figure 12. Filters assembly at Harnaschpolder's Pilot Plant

The following figure (Figure 13) presents a schematic of the lab scale filters that were operated in HNP reuse pilot. A detailed drawing is presented in the Annex section of this document.

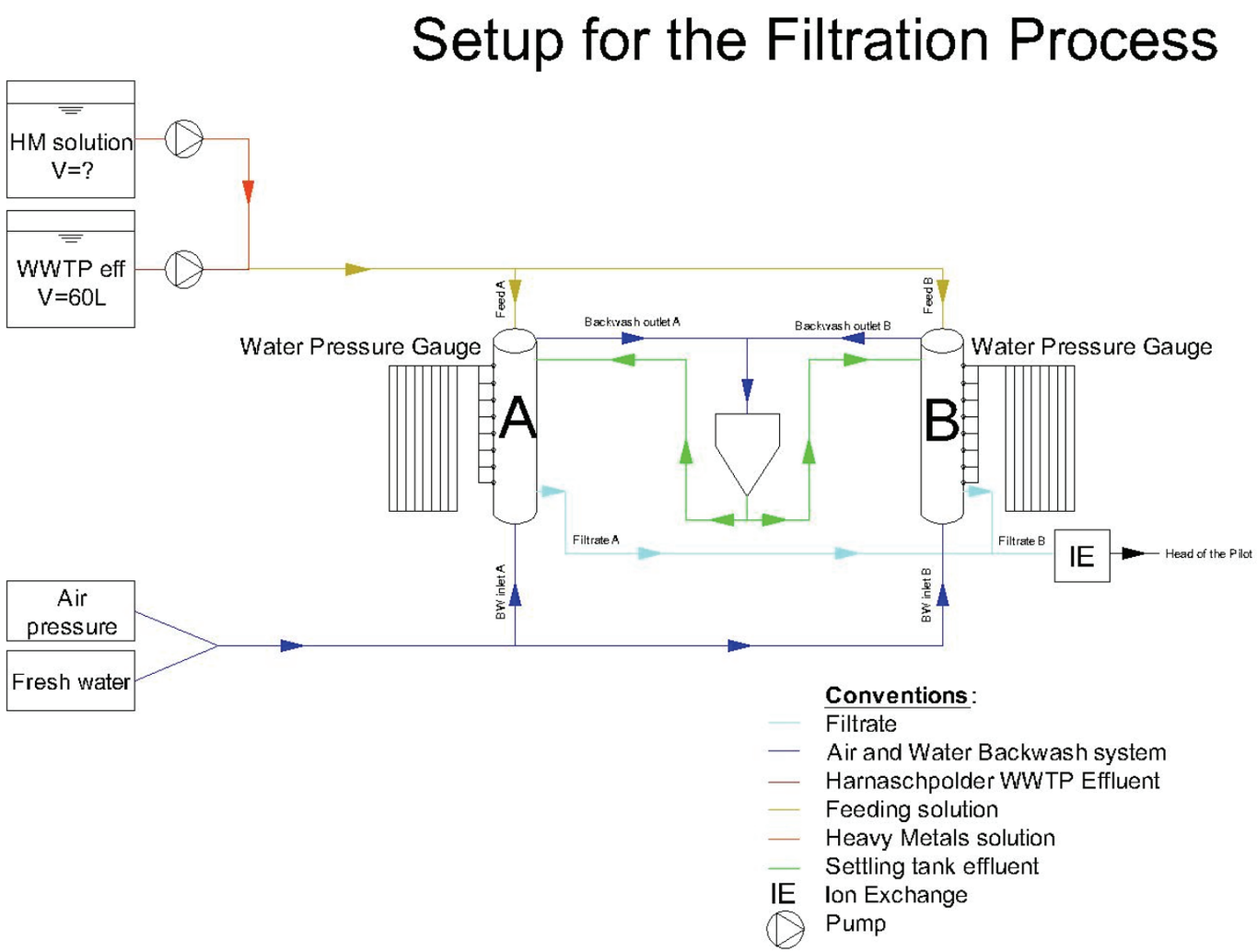

Figure 13. Schematics of the setup for the filtration experiments

To feed each of the dual media filters (labeled as «filter A» and «filter B») two peristaltic pumps were installed. The inlet of each filter was located at 50cm from the top, which was at 250cm of height.

As the feeding water gets into the filter, it moves downwards throughout the filter media into the sewage system (effluent outlet). The outflow (effluent) can be simply altered by regulating the height of the effluent discharge, to prevent that the filter dries. The filter effluent was then treated by ion exchange before being discharged on the sewage to make sure that no heavy metals would pollute the effluent line.

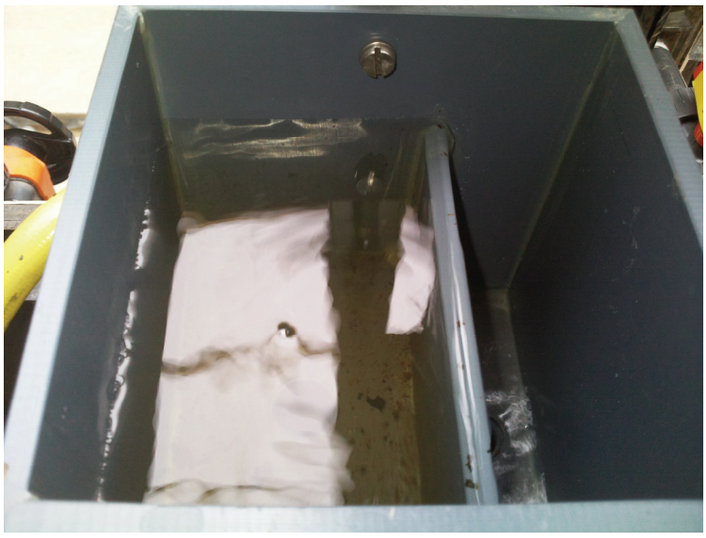

Figure 14. Effluent regulator box

– First run of experiments – «start up»

The «start up» is a very important procedure in order to understand the optimal combination of filter bed depth, particle size (depends of the filter material), filtration velocity and height of the supernatant water (head loss).

According to Miska-Markusch (2009), the optimal combination leads to a filter that is cost efficient and satisfying the required effluent quality resulting in a reasonable filter run time. Additionally, during the filter run the suspended solids should be distributed over the filter bed height to avoid a premature fouling. The filter surface should also be as small as possible, increasing the filtration velocity which can be compensated by increasing the filter bed height (or choosing a different bed material). The backwash time is also evaluated to prevent the deterioration of the water quality due to the increase of water resistance in the medium (Miska-Markusch, 2009) by analyzing the pressure variation in the filters. The following table (Table 10) summarizes the effects of the design parameters (independent variables) on the filters' run.

Table 10. Summary of effects of independent variables on length of filter run (Miska-Markusch, 2009)

Independent Variable	Head loss		Effluent Quality	
	Time	Cumulative volume	Time	Cumulative volume
Depth ↑	↓	↓	↑	↑
Media Size ↑	↑	↑	↓	↓
Velocity ↑	↓	↔	↓↓	↓
Influent Conc. ↑	↓	↓	↓	↓

During the start-up of the filters there were a few problems: the filters were fed by two centrifugal pumps which were not capable to keep a constant flow into the filters. After trying higher flow rates and pump adjustments, the problem was solved by replacing the centrifuge pumps by peristaltic pumps, that are more reliable.

The dosing of heavy metals in both filters was only done after two months of practical adjustments required to solve leakages and desired pumping flows.

– Filters backwash

The backwash was set to be done once the water level achieved 250cm of height in the filter. This means that the running time (period of time between two consecutive backwashes) corresponded to the time between the initial water level (about 200cm) and the maximum water level, 250cm.

At the maximum achieved water level, the maximum filter resistance and turbidity are reached.

The dual media filters were backwashed with both air (at 3bar of pressure) and water (more than 2m of pressure). Before every backwash, all the influent connections were shut down and the respective valves were closed. The backwash procedure started firstly with 1-1.5 minutes of air; then the air supply was closed and then the filter was washed with tap water with a flow rate between 700 and 1000 L/h for 5 minutes. During the backwash with tap-water, air at low flow can also be applied in case of heavy bulking on the top of the filters. The backwash effluent was sent to a buffer tank, followed by ion exchange, before final discharge. Figure 15 presents the backwash system assembled in the lab scale pilot installation.

Figure 15. The backwash system in operation

– Heavy metals dosing and measurements

The dosing of heavy metals was done directly in the feeding pipe from a high concentrated solution of heavy metals that was replaced every two or three days.

The high concentrated solution was prepared with metal chloride compounds in order to obtain final concentrations in the filter of 250µg/L of each metal (Ni, Cd, Cu and Zn).

Table 11 shows the composition of the mother solution that was pumped into filter at 1,25mL/min flow rate, through a peristaltic pump (Watson Marlow Series 200).

Table 11. Heavy metals concentration for mother solution

HM	Metal Chloride	Q_{filter}	HM concentration in the filter		$Q_{dosing\ pump}$		Metal concentration	Fraction of Metal*	Metal Chloride in mother solution
	-	L/h	µg/L	mg/L	L/h	mL/min	mg/L	-	mg/L
Cd	$CdCl_2.nH_2O$ (n=0.5-2.5)	100	250	0.250	0.075	1.25	333.33	0.492	677.03
Cu	$CuCl_2.2H_2O$	100	250	0.250	0.075	1.25	333.33	0.373	894.11
Ni	$NiCl_2.6H_2O$	100	250	0.250	0.075	1.25	333.33	0.247	1349.38
Zn	$ZnCl_2$	100	250	0.250	0.075	1.25	333.33	0.480	694.84

* Fraction of pure metal that is contained in the metal chloride powder

The total and dissolved concentrations of heavy metal (Cd, Cu, Ni and Zn) were determined (in a parallel research) by means of Inductively Coupled Plasma (ICP-MS) for both filters, in three sampling points: input, filtrate and at 85cm bed height (beginning of anthracite layer). A daily composite sample from the input and filtrate were taken for characterization. Also, the COD and NO_3 consumption were analyzed in the filters by *cuvette* tests. The pH, temperature and turbidity concentration were measured as well by hand analyzers. The samples were taken immediately to the water lab located in HNP treatment plant to be analyzed (Table 12).

Table 12. Physicochemical parameters measured in the filters

Parameters	Units
pH	-
Turbidity	NTU
Temperature	ºC
COD	mg/L
NO_3-N	mg/L

The head loss along the dual media filter was also recorded by reading the pressure variation in the manometers located at the side of each filter column.

– Filter operation

The filter operation was divided in two stages: a first stage (blank conditions) without any additions into the filter and a second stage were heavy metals were added. A third stage was further carried out with addition of heavy metals, carbon and metal sorbing bacteria but the analysis and results of this last stage are out of the scope of this research.

As mentioned before, the filters were operated at a constant flow and raised water level. A feed flow of 100 (±5) L/h was used for the operation of the filters, with filtration velocities between 8 and 25 m/h and a hydraulic retention time (HRT) of approximately 10 minutes. During the run time of the filters, the removal of solids and the accumulation of biomass took place on the top layer, as a consequence the filter resistance increased leading to the backwash of the system.

I. First stage: Blank conditions

The filters were run without any additions (heavy metals, carbon) for some weeks. During this period, the turbidity, pressure (head loss), COD and NO_3 was controlled every day for 4 days. The aim of this stage was to check that both filters (A and B) would present the same efficiency since they were operated under the same conditions.

The filter run time (Tr) for this stage was 4 days and the SWL increased to a maximum of 260 cm.

The applied backwash consisted of 5min of tap water at a flow rate of 1000 L/h. Because there was no introduction of HM into the filters, the backwash water was directly discharged in the sewerage system.

II. Filters with addition of heavy metals

After stabilization of both filters as a first stage, Filter A and B were dosed in order to present 250 µg/L of each metal (Cd, Cu, Ni and Zn) in the filter.

Heavy metals, turbidity, COD, NO_3-N, pH and temperature were monitored as in the previous stage.

The filter run time (Tr) for this stage was also 4 days and the SWL increased to a maximum of 210 cm. The applied backwash consisted of 5-7min of tap water at a flow rate of 700 L/h. The backwash effluent was then collected in a settling tank and the supernatant was pumped into the ion exchange system for further discharge in the sewerage system. As stated before, the ion exchange system was used to prevent any contamination of sewage with the added heavy metals.

6. RESULTS AND DISCUSSION

6.1 Results obtained using PHREEQc software

The possibility of metals precipitation during filter experiments was tested to estimate the circumstances in which metal precipitation takes place. Using PHREEQc software, solubility diagrams were then created for each heavy metal in which is represented various solubility curves for each phase of the same metal. The metals used in this simulation represent the ions that are most commonly found in the Harchaspolder's untreated and treated effluent.

– Cadmium equilibrium diagram

The following graph shows the cadmium solubility curves for cadmium (Cd) complex included in the simulation (Figure 16). These metal complexes are manually selected from the program's own database (in this case is the «llnl.dat»). The same procedure was done for the remaining heavy metals.

The yy axis represents the variation of concentration of the cadmium phases while the xx axis represents the variation of pH. Sodium hydroxide was "virtually" dosed to simulate the variation of pH in this graph (Figure 16).

The cadmium phases that are most likely to precipitate under the filters conditions are cadmium hydroxide ($Cd(OH_2)$), cadmium carbonate ($CdCO_3$, also known as «otavite»), cadmium sulfite (CdS) and cadmium phosphate ($Cd_3(PO_4)_2$).

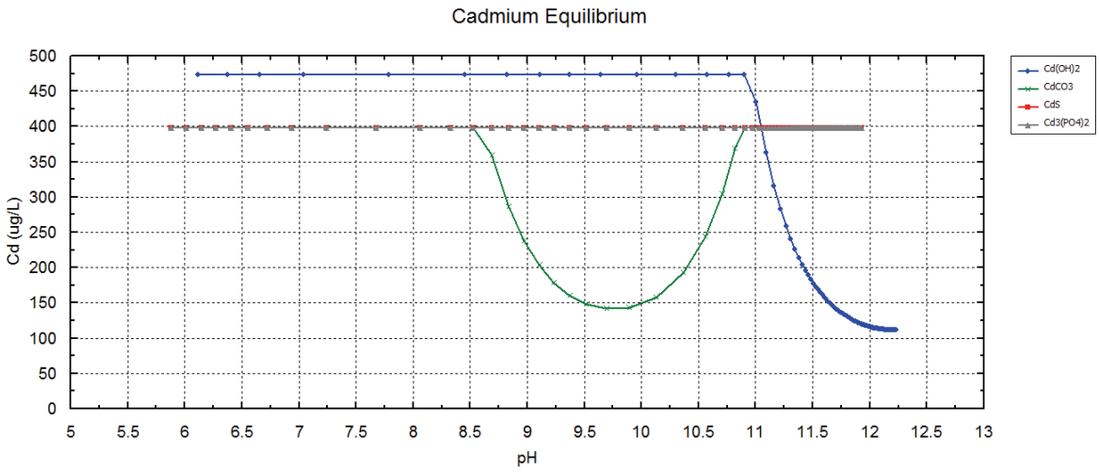

Figure 16. Cadmium equilibrium diagram

According to the graph above, most of the cadmium complexes tend to precipitate at high values of pH. From this graph, it is possible to see that cadmium sulfite and cadmium phosphate appear to have no changes in their solubility for all the pH range, meaning that these two phases remain soluble regardless of the pH variation in the final solution.

On the other hand, the other two forms of cadmium present in this «mixed water» – cadmium hydroxide and cadmium carbonate – show possible precipitation from pH above neutrality, which means that they only precipitate in alkaline environments, according to the graph above. According to the graph, cadmium carbonate starts to precipitate from pH values close to 8.5, reaching maximum precipitation at pH=9.75 (approximately) and ceasing to precipitate at pH=11 (approximately). However, cadmium hydroxide only precipitates at pH values greater than 11, meaning that these two species don't coexist in the solution. Maximum precipitation (for cadmium hydroxide) is achieved at maximum pH levels possible ($12 < pH < 12.25$). The results obtained in this simulation are coherent with the bibliography (chapter 3, Figure 3), which confirms that the cadmium hydroxides do precipitate in the presence of alkaline solutions (pH=11-12).

According to the filter analysis during the first stage of the filter operation, a removal of 86% for this metal was achieved. This suggests that the removal observed in the filters was mostly physicochemical rather than biological. With no inoculation of bacteria in the filters nor carbon source it is very unlikely to remove HM biologically.

However, since the pH of the HNP effluent was slightly acidic, most of the removal wasn't caused by physicochemical precipitation but by another process probably by adsorption in the anthracite layer, according to the bibliography (Benjamin *et al.*, 1982).

In the filters with inoculation of heavy metals (and carbon), when carbon is metabolized by the bacteria is generates alkalinity, thus increasing the pH and promoting chemical precipitation. However, the pH values in the filter remained largely constant at 6.85 meaning that metal precipitation mechanisms (as metal hydroxides and carbonates) are unlikely to occur in the operating conditions.

The simulation showed that possible precipitation occurred at high levels of pH, *i.e.* in an alkaline environment. However, during the filter operation, the pH remained slightly under the neutrality (6.85) and there were no «optimal conditions» for occurring chemical precipitation of cadmium.

This way, the removal occurred in the filter suggests that there were involved some adsorption mechanisms into the filter material or into the bacteria already present in the wastewater that may serve as an adsorbent.

– Copper equilibrium diagram

The following graph shows the copper solubility curves for each complex of copper that can be formed with the ions present in the wastewater.

The *yy* axis represents the variation of concentration of the copper phases while the *xx* axis represents the variation of pH. Like the previous graph (cadmium), sodium hydroxide was «virtually» dosed to simulate the variation of pH in this graph (Figure 17).

Unlike cadmium, some phases of copper such as carbonates and hydroxides appear together in the same compound, under certain conditions; *i.e.* minerals such as «*azurite*» ($Cu_3(CO_3)_2(OH)_2$) and «*malachite*» ($Cu_2CO_3(OH)_2$) may be formed according to the simulation. The remaining forms that were also tested for precipitation in this simulation were copper sulfite (CuS, also known as «*covellite*») and copper phosphate ($Cu_3(PO_4)_2$). These four compounds are represented in the following graph:

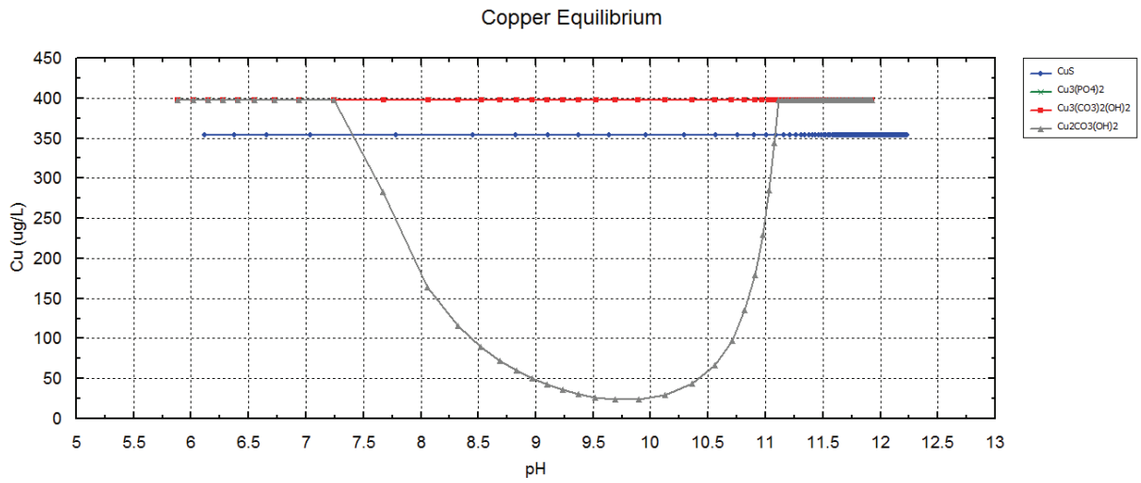

Figure 16. Copper equilibrium diagram

According to the graph above, it is clear that most of the copper phases don't have any reaction, under the simulation conditions; *i.e.* their solubility remains unchanged while pH increases gradually. The majority of the forms shows no changes in their solubility for all the pH range, meaning that these three phases remain soluble (high concentration solubility values) regardless of the pH variation in the final solution.

On the other hand, the only form of copper present in this «mixed water» appears to be «*malachite*» (the grey line), where possible precipitation starts slightly above the neutrality point (pH=7.25, approximately) and the solubility decreases along the increase of pH. Precipitation achieves maximum values at pH of 9.5-10 and decreases gradually until achieves a maximum pH of approximately 11, according to the graph.

According to the bibliography in the «Literature Review» chapter, the results obtained in this simulation are discordant. The precipitation of copper hydroxide (or «*malachite*»),in the graph above, is similar to the chemical precipitation portrayed in the literature review. According to Wang *et al.* (2006), the precipitation of copper hydroxide compounds occurs in a pH from 6 to 12. This compound is most insoluble when pH values are near 9-10 (Wang *et al.*, 2006), which also happens in the simulation.

On the other hand, «*covellite*» (or copper sulfite), according to the literature, which tends to precipitate at an optimal pH of 6.8 doesn't show any difference in the solubility curves in the simulation. This may point out the fact that other processes of copper precipitation may be involved in the simulation like adsorption into the filter or maybe adsorption into the bacteria.

According to the filter experiments, with no carbon dosing, an average of 72% and 60% of removal efficiency was achieved for dissolved and total copper, respectively. The experimental results are contrary to the bibliography. In Miska-Markusch (2009) experiments, when carbon is dosed, the removal efficiency of the fraction of the total inorganic copper content is 85%, compared to 66% when there is no dosing . In the HNP experiments (no carbon is dosed), both forms of copper were highly removed although the dissolved copper removal efficiency was slightly higher.

Table 13. Percentage of copper removal from filtration tests (adapted from Miska-Markusch, 2009)

With methanol		Without methanol	
Total	Dissolved (< 0.45µm)	Total	Dissolved (< 0.45µm)
85%	40%	66%	80%

Copper removal showed a similar behaviour as cadmium, which was removed (in the filter) by physicochemical processes rather than biological. However, since the pH of the medium was slightly acidic, most of the removal wasn't caused by physicochemical precipitation because the pH at the present simulation showed that precipitation occurred at pH=7.25. There may be some traces of «*malachite*» precipitates since the pH difference is not significant, but other processes of copper removal may be involved in the reaction (*e.g.* metal adsorption in the filters' anthracite layer).

The simulation, which was done for the same conditions as the filter experiments, showed that possible precipitation occurred at high levels of pH, *i.e.* in an alkaline environment. This was not the case in the filter experiments, which the pH remained slightly under the neutrality (6.85) and there were no «optimal conditions» for occurring chemical precipitation of copper.

– Nickel equilibrium diagram

The following graph shows the nickel solubility curves for each phase of nickel (Ni) present in the simulation. The *yy* axis represents the variation of concentration of the nickel phases while the *xx* axis represents the variation of pH, according to the dosing of the sodium hydroxide (Figure 18).

The nickel phases that are most likely to precipitate under the filters conditions are nickel carbonate ($NiCO_3$), nickel hydroxide ($Ni(OH)_2$), nickel orthophosphate ($Ni_2P_2O_7$), nickel phosphate ($Ni(PO_4)_2$) and nickel sulfite (NiS, also known as «*millerite*»).

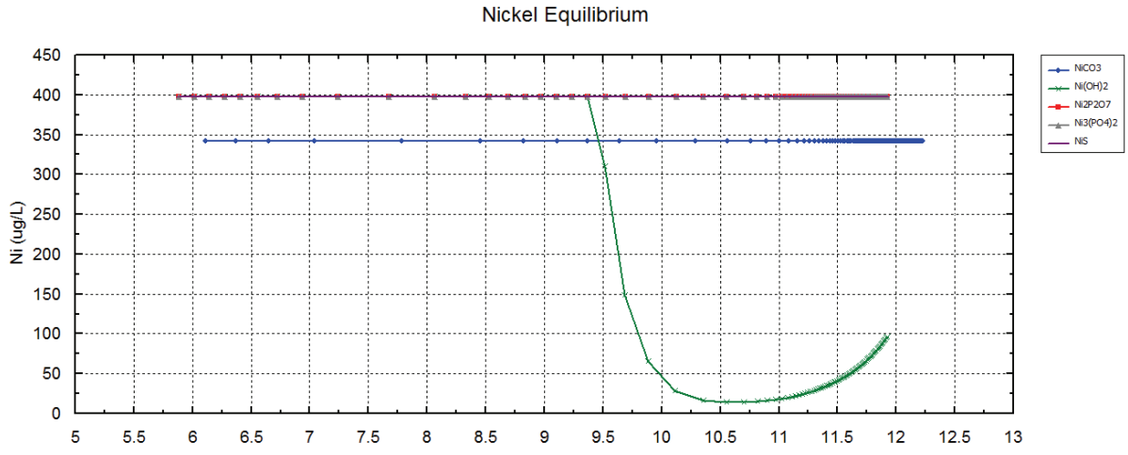

Figure 18. Nickel equilibrium diagram

According to the graph above, it is clear that the majority of nickel forms remain unaltered during the simulation. The only form of nickel that shows an apparent reaction is nickel hydroxide. From the graph above, it is possible to observe that this nickel form tends to precipitate at high values of pH, following the same pattern as the previous simulations. The remaining forms: nickel carbonate, nickel phosphates and nickel sulfite remain unchanged in terms of solubility. This means that throughout all of the pH range, the various forms of nickel precipitates remain soluble in the solution.

On the other hand, the only nickel form that shows possible precipitation, under the simulation (and filter conditions), is nickel hydroxide ($Ni(OH)_2$). From the graph, it is possible to see that this form precipitates under alkaline conditions, more precisely under the pH range from 9.25 until 11.8 (approximately). Precipitation for nickel hydroxide increases as increasing pH, reaching a maximum at pH=10.5-11. For further values of pH, solubility values tend to increase thus decreasing its precipitation.

According to Wang *et al*. (2006), precipitation of nickel hydroxides typically occurs in a short interval of pH values (9-12) whilst in this simulation occurred in a slightly wider range of values, from 9.5 to 12 (Wang *et al*., 2006).

As for nickel sulfite, in the simulation showed no apparent variation of solubility while literature suggests that most of the precipitation occurs in a wide range of pH, achieving maximum precipitation at pH of 11.

Although the author suggests these values for a specific type of metal removal – chemical precipitation – there are other mechanisms of removal that may present different values, namely chemical adsorption of chelation for example.

According to the filter experiments, with no carbon dosing, an average of 30% of removal efficiency was achieved for both dissolved and particulate nickel. The experimental results are different than the results stated in the bibliography. In Miska-Markusch (2009) experiments, the removal of nickel occurs mainly when methanol is dosed in the particulate form rather than the dissolved form. The combined removal is approximately 50%. When methanol is not dosed, the fraction of dissolved nickel even increases. In the HNP experiments, both forms of nickel were highly removed although higher in the dissolved form.

Table 14. Percentage of nickel removal from filtration tests (adapted from Miska-Markusch, 2009)

With methanol		**Without methanol**	
Total	Dissolved (< 0.45µm)	Total	Dissolved (< 0.45µm)
30%	25%	<1%	-20%

However, since the pH of the medium was slightly acidic, most of the removal wasn't caused by physicochemical precipitation but probably by another process such as metal adsorption in the filters' anthracite layer as stated previously. This layer of carbon may have served as an physicochemical adsorbent for heavy metals (Barakat, 2011). Also, there may occur some adsorption due to the existence of bacteria present in the wastewater (Davis *et al*., 2007, Vanbroekhoven *et al*., 2007).

The simulation, which operated under the same conditions as the filter experiments, showed that possible precipitation occurred at high levels of pH, *i.e*. in an alkaline environment. This was not the case in the filter experiments, which the pH remained slightly under the neutrality (6.85) and there were no "optimal conditions" for occurring chemical precipitation of nickel.

– Zinc equilibrium solubilities

The following graph shows the zinc solubility curves for each complex of zinc (Zn) present in the simulation. The *yy* axis represents the variation of concentration of the zinc phases while the *xx* axis represents the variation of pH, according to the dosing of the sodium hydroxide (Figure 19).

The zinc phases that are most likely to precipitate under the filters conditions are zinc carbonate ($ZnCO_3$, also known as «*smithsonite*»), zinc sulfite (ZnS, also known as «*sphalerite*»), zinc carbonate monohydrated ($ZnCO_3.H_2O$) and zinc hydroxide ($Zn(OH)_2$).

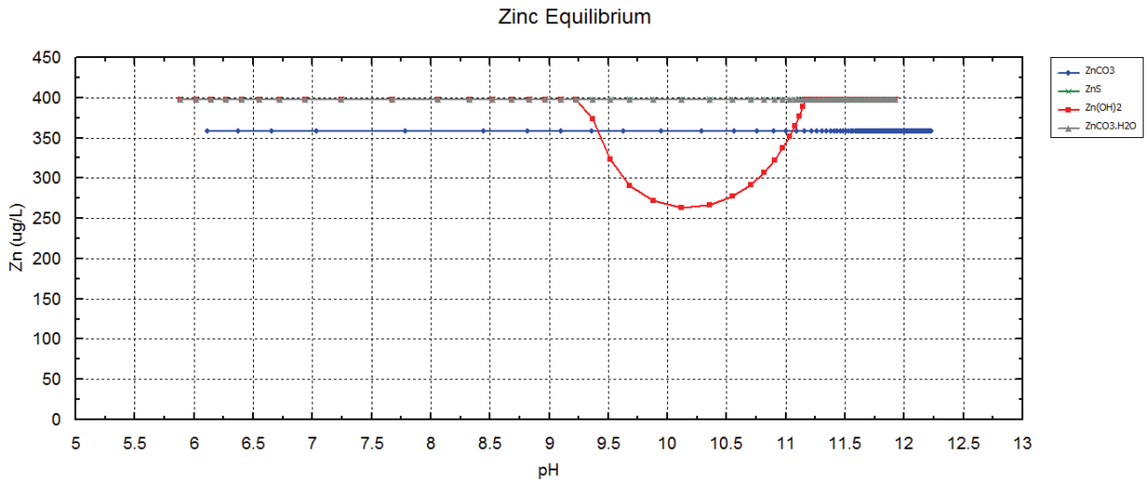

Figure 19. Zinc equilibrium diagram

According to the graph above, the zinc phases tend to precipitate in an alkaline environment, following the same pattern as the previous metals. From the graph above, it is possible to observe that the majority of zinc phases (zinc carbonate or «*smithsonite*», zinc sulfite or «*shparelite*, zinc hydroxide and zinc carbonate monohydrated) remain unchanged in terms of solubility for all the pH range, *i.e.* these forms remain soluble throughout the entire pH range and are unable to precipitate under the conditions of the simulation.

On the other hand, the only zinc form that appears to show possible precipitation is zinc hydroxide ($Zn(OH)_2$). From the graph, it is possible to see that this form precipitates under alkaline conditions, more precisely under the pH range from 9.25 until 11.2 (approximately). Like nickel, precipitation for zinc hydroxide increases as increasing pH, reaching a maximum at pH=10.1. For further values of pH, solubility values tend to increase thus decreasing its precipitation until reaching a minimum precipitation at pH=11.25.

According to the literature (chapter 3, Figure 3), precipitation of zinc hydroxides typically occurs in an interval of pH values between 9.25 and 11.2, while in the simulation it occurred in a slightly wider range of values (8.5-12 approximately). As for zinc sulfite (or «*spharelite*»), the simulation showed no apparent variation of solubility while bibliography suggests that most of the precipitation occurs in a wide range of pH, achieving maximum precipitation at pH of 11 and a minimum at a pH of 3.

According to the filter experiments, with no carbon dosing, an average of 76% of removal efficiency was achieved for zinc. The experimental results are different than the results stated in the bibliography. In Miska-Markusch (2009) experiments, the removal of zinc occurs mainly when methanol is dosed, and the metal is in the particulate form (total) rather than the dissolved form. The combined removal is approximately 50%. When methanol is not dosed, the fraction of dissolved nickel even increases. In the HNP experiments, both forms of zinc were highly removed although higher in the dissolved form.

Table 15. Percentage of zinc removal from filtration tests (adapted from Miska-Markusch, 2009)

With methanol		**Without methanol**	
Total	Dissolved (< 0.45µm)	Total	Dissolved (< 0.45µm)
33%	15%	0%	-20%

In the filters with inoculation of heavy metals (and carbon), when carbon is metabolized by the bacteria found in the treated wastewater, it generates alkalinity. Thus, increasing the pH of the media and promoting some form of chemical precipitation (whether is hydroxide precipitation, sulfite, etc.). However, alkalinity is only generated when acetate is dosed instead of methanol, meaning that bacterial precipitation did not occur in the filters.

The pH values in the filter remained largely constant at 6.85 meaning that zinc precipitation mechanisms (as zinc hydroxides mainly) are unlikely to occur in the operating conditions.

The simulation, as the filter experiments, showed that possible precipitation occurred at high levels of pH, *i.e.* in an alkaline environment. This was not the case in the filter experiments, which the pH remained slightly under the neutrality (6.85) and there were no «optimal conditions» for occurring chemical precipitation of zinc.

The simulations for all metals were obtained considering HNP effluent characteristics with no addition of carbon source within the filters. Due to limitations of the program, the use of methanol could not be considered in the solubility curves simulations.

6.2 Removal of heavy metals in the filters

Heavy metals appear in HNP effluent through various diffuse sources and are present in dissolved and total form. For the present research the focus was on the removal of Cd, Cu, Ni and Zn, a major part

of these metals are already removed due to previous process treatments in HNP WWTP (primary and secondary treatment), however their removal is not complete and do not meet the most stringent MTR levels in the Netherlands. Therefore, it was part of this research to find what physicochemical mechanism should be expected after dosing concentrations between 120-150µg/L of Cd, Cu, Ni and Zn in the dual media filter.

The two dual media filters (A and B) were operated in two consecutive stages. In these stages, measurements on pressure loss, turbidity and heavy metals were performed:

I. Filters with no addition of heavy metals nor carbon;
II. Filters with addition of heavy metals without carbon.

For both stages pressure, turbidity and heavy metals removal were monitored.

– Pressure readings

The end of the filter run (Tr) is reached when the suspended solids in the effluent start to increase (breakthrough) beyond an acceptable level, or when a limiting head loss occurs across the filter bed.

When the suspended solids in the effluent start to increase beyond an acceptable level, or when a limiting head loss occurs across the filter bed, the filtration phase is terminated, and the filter must be cleaned (Metcalf & Eddy *et al.*, 2003). Accumulation of solids which are distributed over the complete filter bed is called deep bed filtration. When accumulation only occurs at the top of the filter bed it is called cake filtration (Metcalf & Eddy *et al*., 2003).

The increase in resistance in the filter bed for the dual media filters was measured through pressure readings. The increasing pressure drop presented through Lindquist diagrams, which show pressure loss against filter bed height in time. Pressure readings were obtained through manometers connected to the filters.

The *yy* axis shows the filter bed height (in cm) and the *xx* axis presents the pressure in cmWC (cm of Water Column). Different run times (Tr) are presented in the graph (Villarroel Toral, 2011, Metcalf & Eddy *et al*., 2003).

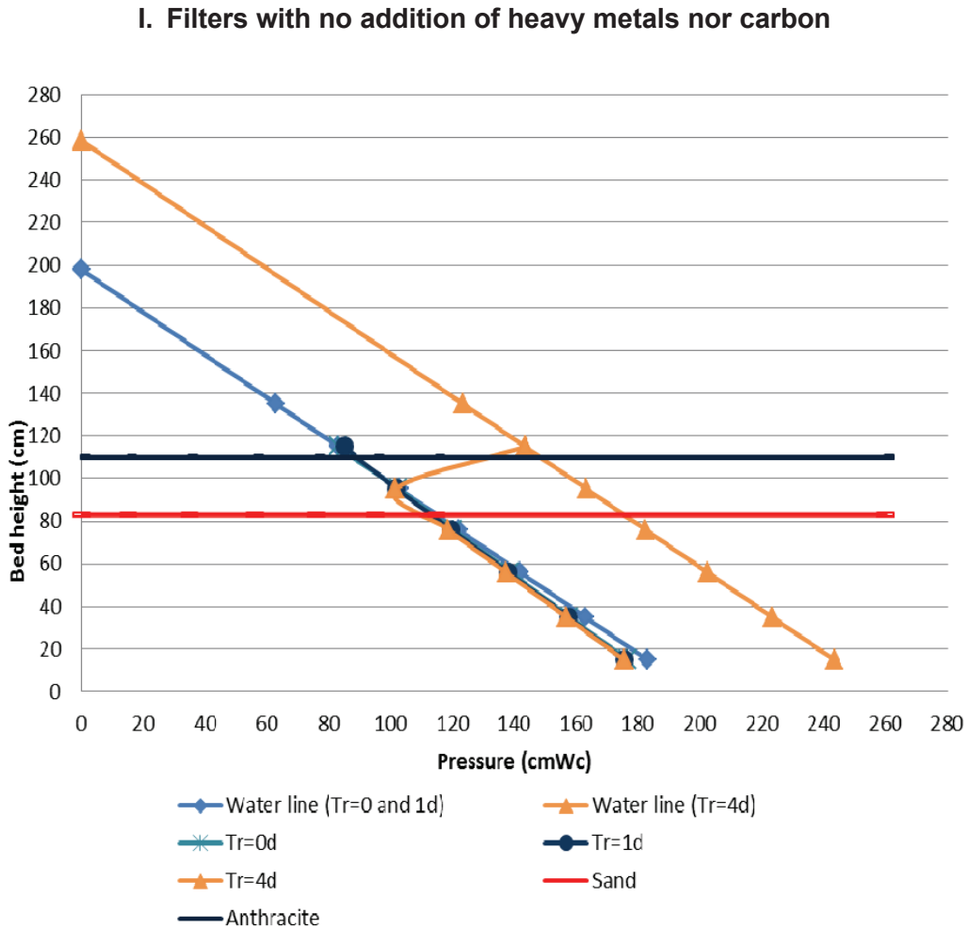

Figure 20. Lindquist diagram for the dual media filter during filter run time for both filters A or B (Villarroel Toral, 2011)

Figure 20 shows that the pressure increased in the first and the last day of the filters' run time period. There was a pressure increase during the run time period, when clogging was observed on the anthracite layer just above the sand layer. As the filters were not dosed with heavy metals (the only source of HM is the treated wastewater), bacterial growth in the filters should be minimal. Therefore, the filters were able to work for a prolonged period of time without being backwashed. The SWL increased by 60 cm during a period of 4 days, period which was considered as «*Tr*». Therefore, it was established that whenever the filters reached a SWL of 260cm, the filters were backwashed. By observing the results from the Lindquist diagrams for both filters, it can be concluded that both filters have equal hydraulic performance during this phase, this was considered as the filter stabilization phase, where all hydraulic parameters such as initial flow rate, filtration velocity, outflow rate and HRT where fixed in order to have both filters running under the same conditions.

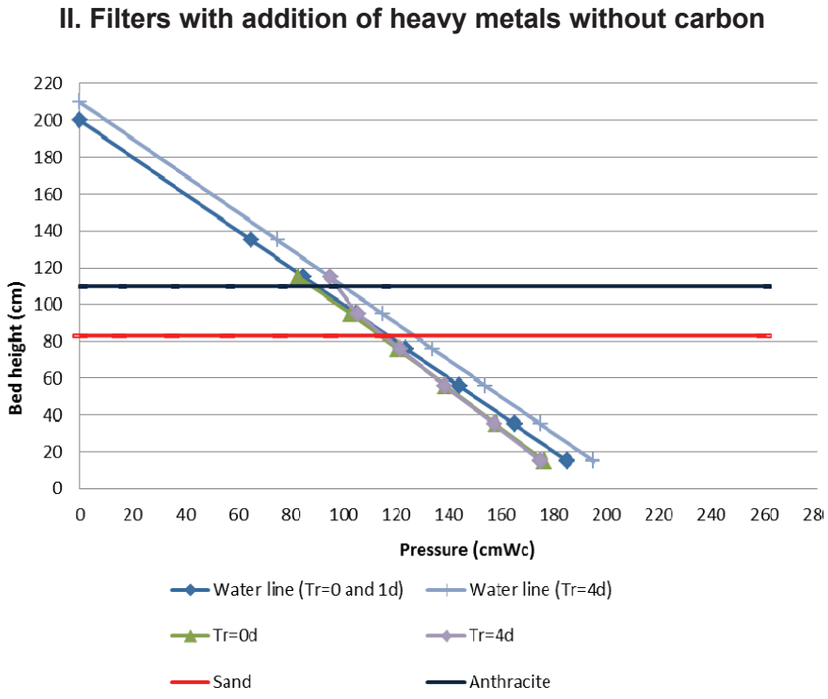

Figure 21. Lindquist diagram for the filters A or B, during filter run time with addition of HM (Villarroel Toral, 2011)

Figure 21 shows the typical curve of pressure increase during the first and last day of the filters run time. Results show that there was not a clear increase in the filter bed resistance during the filters run time.

Therefore, another graph was constructed in order to show the increase of head loss in time (Figure 22).

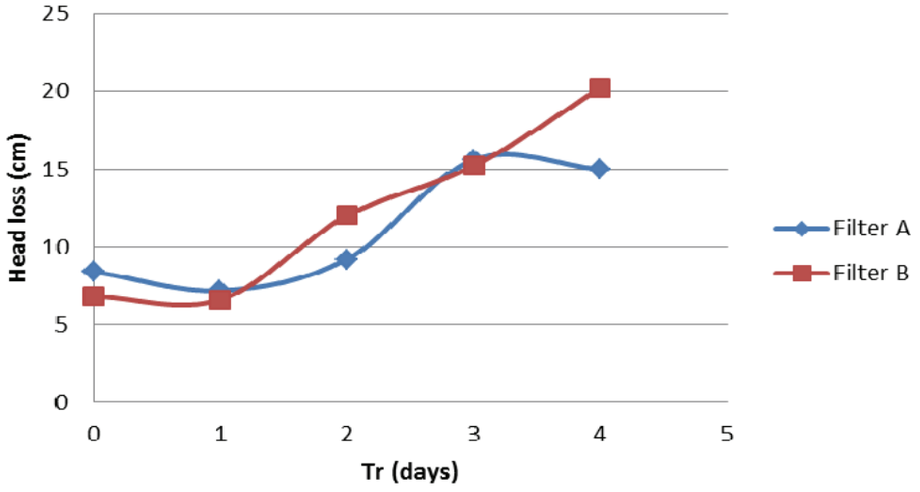

Figure 22. Increase in head loss in filters with no addition of heavy metals (nor carbon) (Villarroel Toral, 2011)

In the figure above, it is visible that there was a gradual increase in head loss (due to the increase of clogging), meaning that the filtration process was occurring normally. The majority of the resistance was built up in the upper part of the filter, in the anthracite layer. The SWL increased by 10 cm during a period of 4 days, which was considered as «Tr». Therefore when the filters reached a SWL of 210 cm, the filters were backwashed.

– Turbidity

The TSS concentration in the effluent is the principal parameter of concern because it is a simple way of knowing if the water is rich with suspended solids such as minerals, organic matter, etc. It can also contain some heavy metal compounds that may influence the outcome of the experiments and the good or bad performance of the filters.

Therefore, turbidity was used in this research as an overall indicator for filtration efficiency. Corresponding turbidity values can vary from 3 to 15 NTU (Metcalf & Eddy *et al*., 2003) (see Figure 23 to Figure 26).

I. Filters with no addition of heavy metals nor carbon

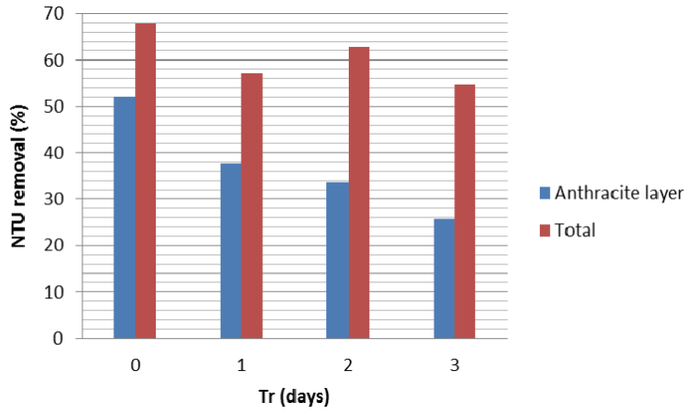

Figure 23. Turbidity removal with no addition of heavy metals nor carbon (Filter A) (Villarroel Toral, 2011)

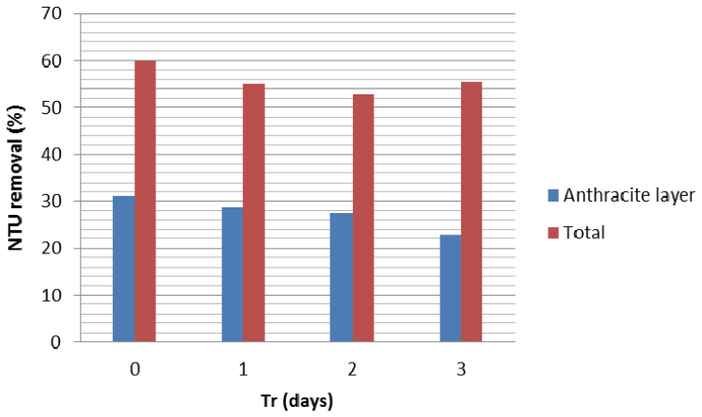

Figure 24. Turbidity removal with no addition of heavy metals nor carbon (Filter B) (Villarroel Toral, 2011

According to Figure 23 and Figure 24, it is possible to see that occurred high removal of turbidity in the anthracite layer, which could indicate a cake filtration on the top layer of the filter. The removal in the anthracite layer went from 52% in the first day until 26% on the third day, for Filter A; while for Filter B it went from 31% to 23%. On the other hand, the total turbidity removal through Filter A went from 68% to 55% and Filter B from 60% to 55%, during the 4 days of filter run time.

II. Filters with addition of heavy metals without carbon

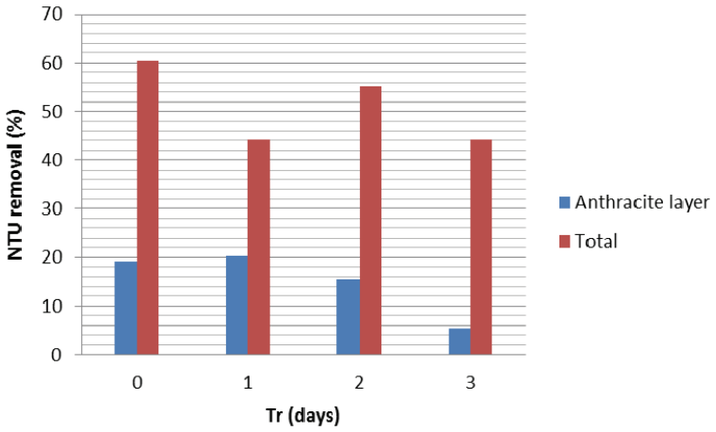

Figure 25. Turbidity removal with addition of HM for Filter A (no carbon) (Villarroel Toral, 2011)

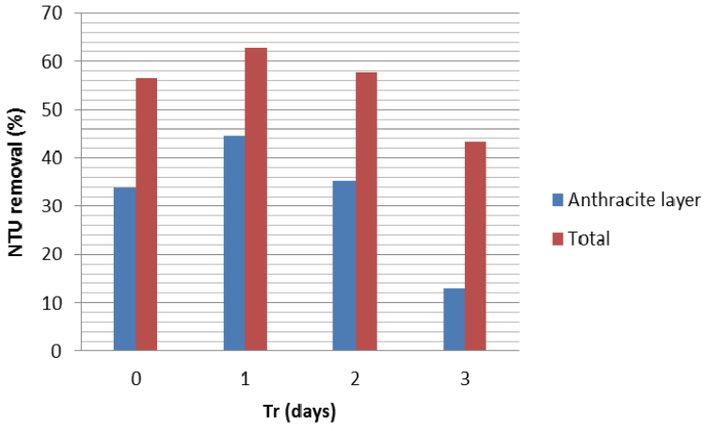

Figure 26. Turbidity removal with addition of HM for Filter B (no carbon) (Villarroel Toral, 2011)

According the graphs above, Figure 25 and Figure 26, it can be observed that a major part of the removal of turbidity was performed by anthracite layer during filters' run. The turbidity removal efficiency decreased during filter run time in the anthracite layer, the removal in the anthracite layer went from 19% in the first day until 6% on the third day, for Filter A; while for Filter B it went from 34% to 13%. On the other hand, the average for the total turbidity removal through Filter A was 51% and Filter B 55%, for the

4 days of filter run time, meaning that overall the filtration process is working as expected. The differences of turbidity removal through the anthracite layer between Filter A and Filter B, could be due to the higher accumulation of solids and biomass in the top layer of one of the filters concerning cake filtration.

– Heavy metal removal

In the first stage of experiments, there was no dosing of heavy metals. Therefore, there were no samples taken for ICP analysis was not carried out.

Both filters were dosed with Cd, Cu, Ni and Zn in order to have an initial concentration of 250 (±10) µg/L of each metal in the filters. The removal efficiency was calculated based on the initial (HM dosing) and final concentrations (ICP analysis).

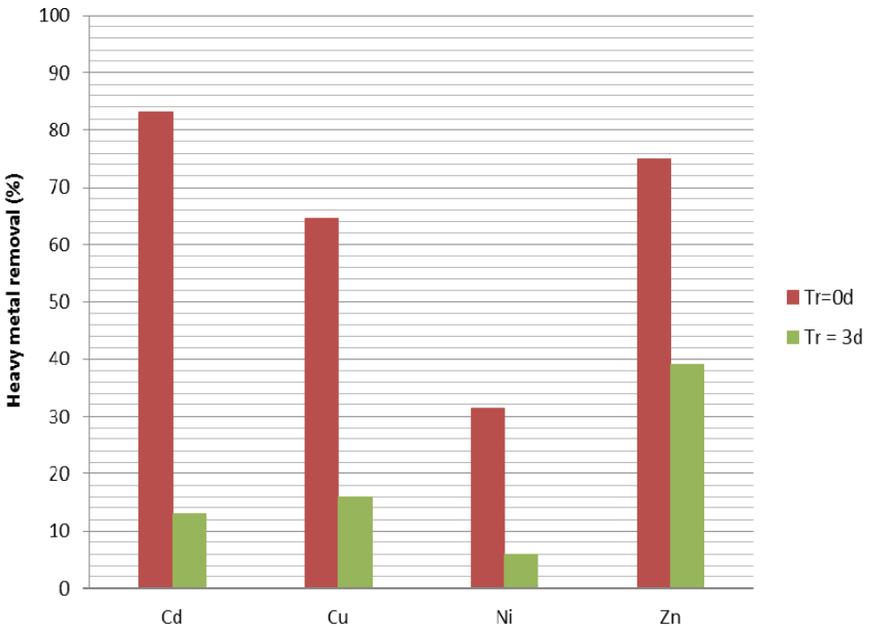

Figure 27. Dissolved HM removal with addition of HM – Filter A (Villarroel Toral, 2011)

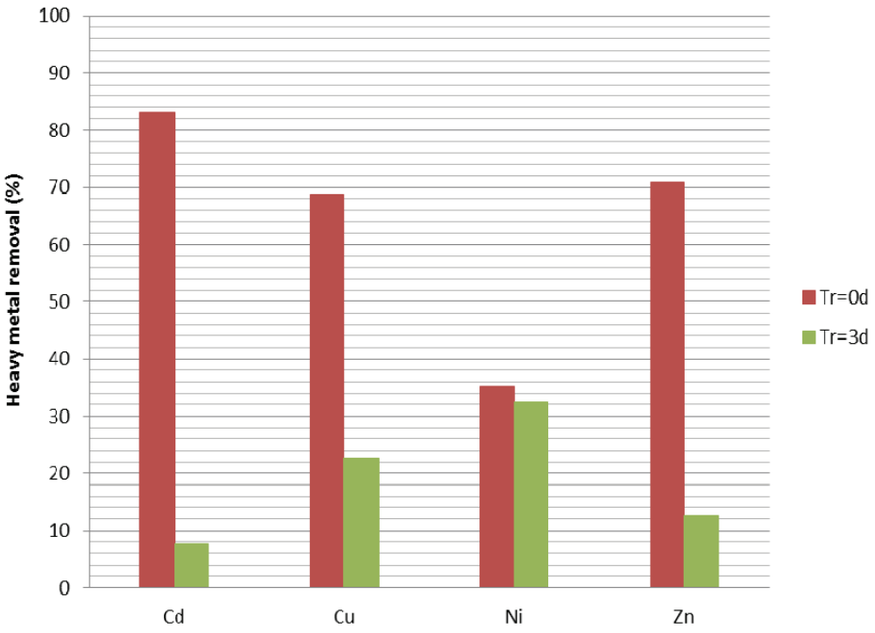

Figure 28. Dissolved HM removal with addition of HM – Filter B (Villarroel Toral, 2011)

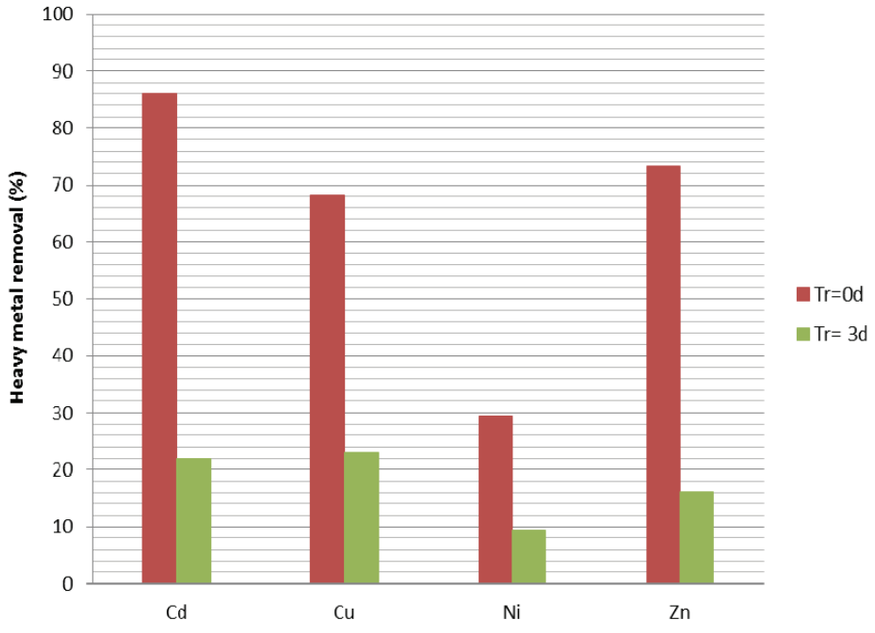

Figure 29. Total HM removal with addition of HM – Filter A (Villarroel Toral, 2011)

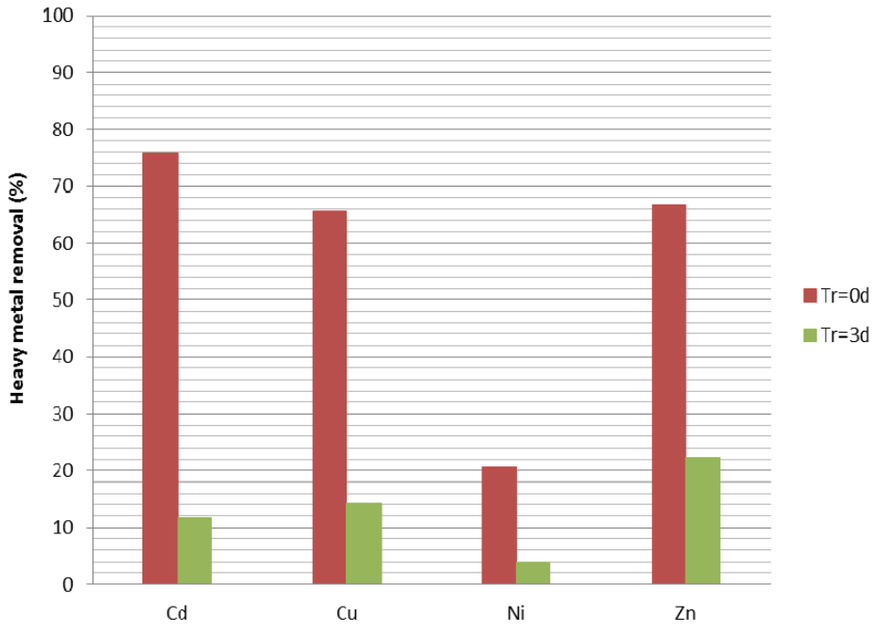

Figure 30. Total HM removal with addition of HM – Filter B (Villarroel Toral, 2011)

The removal of total and dissolved metals are comparable for both filters, results obtained from ICP measurements showed that there was no significant difference between the concentrations of total and dissolved metals (Cd, Cu, Ni and Zn) especially at the beginning of the run time period. A possible reason for this could be that all metals were mostly presented in a dissolved form.

From Figure 27 to Figure 30, it is possible to observe that there was an overall removal of heavy metals through the filters. The removal for all metals was higher at the beginning of the filter run period (Tr=0d) than at the end (Tr=3d), from which it can be postulated that the removal of heavy metals decreased with the increase in head loss loss (for a certain period). This indicates that adsorption of heavy metals can occur in the beginning and when the filter gets saturated their removal starts decreasing.

The removal of Cd, Cu, Ni and Zn for Filter A and B, as for dissolved and total was in average 82%, 67%, 29% and 71% respectively, at the beginning of the filter run. After 3 days of filter run a decrease in the removal of metals was observed, showing a removal of dissolved Cd, Cu, Ni and Zn of 13%, 16%, 6%, 39% and total of 22%, 23%, 9% and 16% respectively for Filter A. Whereas for Filter B the removal for dissolved was 8, 23, 32 and 13% and total 12%, 14%, 4% and 22% respectively.

The biomass growth in this stage was negligible due to absence of a carbon source. The aim of having both filters working under the same control conditions was to test the efficiency on heavy metals removal from the dual media filters without any influence of biomass. The high removal of heavy metals in this stage was unexpected, because it was supposed to achieve higher removal of HM when the filters were inoculated with bacteria.

Also, the observed removal efficiency for heavy metals in the filters is apparently not dependent on biomass accumulation or growth. Based on ICP measurements it was confirmed that the initial concentration of each heavy metal in the filter was 250 (±10) µg/L and by analyzing the graphs (Figure 26 to

Figure 29) a high removal efficiency of dissolved and total Cd, Cu, Ni and Zn is observed for both filters. This emphasizes the possibility of HM removal by other mechanisms than chemical precipitation, such as filtration, adsorption and/or ion exchange in the filter medium.

It was also observed that the heavy metals removal efficiency for both filters decreased with the increase in head loss during time. From the graphs above, it was clear that on Tr=0d the HM removal was high and on Tr=3d (last day of filter run time) the removal of HM drastically decreased. It is probable that this phenomenon is due to the overall decrease in filtration performance during time because of the increase in bed resistant by clogging.

7. CONCLUSIONS

7.1 PHREEQc Simulation

Regarding the PHREEQc simulation it was clear that in the filters environment (pH, temperature, ions and heavy metals) chemical precipitation did not occurred as the main process of heavy metal removal mainly because these processes happen in alkaline environments, where the solubility is minimum. The average pH registered in the filter experiments was 6.85, meaning that the medium was slightly acidic. In this conditions, any precipitation is unlikely to happen with the exception of «*malachite*» – copper hydroxide-carbonate, that is the only complex that may precipitate at near-acidic conditions. However, the precipitation for this phase is not optimal, meaning that its solubility is still at very high levels. The «optimal conditions» for precipitating «*malachite*» is achieved at pH of 9.5-10 in which the solubility values are the its lowest.

In both filters, it was not certain what process was involved in heavy metal removal. The only process that was studied in this research – chemical precipitation – shows that there was no optimal conditions (in terms of pH, solubility and temperature) for this process, according to the PHREEQc simulation. Therefore, it is suggested that other processes, namely chemical adsorption, may be involved in HM removal. The anthracite layer in the filter may have served as physicochemical adsorbent for heavy metals due to its properties (Barakat, 2011, Bansal *et al.*, 1988), which might explain the high removal efficiencies obtained in the beginning of the filtration experiments.

7.2 Filter Experiments

There is a lack of knowledge concerning experiments involving the removal of heavy metals from treated domestic wastewater in dual media filters with inoculation of specific bacteria. Regarding the removal of heavy metals from wastewater through bacterial activity, several references can be found in numerous literature, while references to filter-scale experiments are much more scarce.

In the filters dosed with heavy metals, although there wasn't any carbon dosing, the HM removal efficiency doesn't appear dependent on biomass accumulation or growth. Anyhow, high removal efficiency of dissolved and total Cd, Cu, Ni and Zn was obtained for both filters. From the results obtained from both filter experiments and PHREEQc simulation, it can be concluded that in the absence of any carbon source (such as methanol or acetate), a mechanism such as adsorption (in the anthracite layer of the filters) was the major process contributing to heavy metal removal rather than chemical precipitation that it was thought out to be. The pH of the filter medium was too low for chemical precipitation – process of which obtains higher removal performance at alkaline environments.

Also, there might be some denitrifying bacteria that are present in the wastewater (whenever there is carbon present) and serve as an adsorbent matrix for the heavy metals.

Since the conditions for chemical precipitation (or biological uptake by the bacteria or other organisms present in the wastewater) were not optimal, it is plausible that the removal of heavy metals was performed by the anthracite layer.

It is also important to note that the length of the experiments was very short. The run time was too little for both filters (with and without HM dosing). Firstly, due to some flow variations in the plant (inflow valves) and other factors, it took a lot of time to get the filters stabilized and running normally. Second, there was no enough time to understand and to determine if the removal was biological or physicochemical and in what extent.

8. FURTHER RESEARCH RECOMMENDATIONS

8.1 PHREEQc Software Simulation

The use of PHREEQc software throughout this research was proven to be extremely difficult, due to the lack of studies concerning this subject. There are only a few studies that refer the use of this type of software, although they are not explored very deeply. In addition, the program is not very «user-friendly» making extremely difficult and arduous to write the input files correctly, without making any mistakes.

Also, the manual provided with this software is very generic and does not provide any specific procedure regarding its application in water and wastewater treatment. Therefore, the use of this program is subjective, meaning that there are multiple ways of dealing with the problem at hand.

For further studies, not only should be tested other ways of tackling the problem such as making other input files using other commands but also other programs than PHREEQc software should be used. Also, PHREEQc uses batch reactions which are not accurate for this type of simulations and also may contribute to a different reality. Therefore, programs that use flows in their input files (instead of static solutions) are more suitable for this type of simulations giving a better «view» of reality.

8.2 Filter experiments

So far, not enough studies are being conducted to elucidate the removal mechanisms and consequent efficiencies of dual media filtration in removing heavy metals to very low levels like the ones for water reuse as surface water. Therefore, a further study on the removal of heavy metals of treated effluent in a dual media is recommended. In order to define the mechanism responsible for heavy metals removal within the filters and the influence in heavy metals removal, other different mediums types should be tested (including the combination of mediums as well) and also increasing the length of the experiments in order to provide more reliable data.

Hence, it is recommended to develop a feasible, low cost and efficient dual media filter design, which will be capable of reaching ultra low heavy metals concentrations in effluents for reuse and other purposes.

Also it is recommended to continue further studies of other physicochemical processes of heavy metal removal such as filtration, adsorption and/or cation within the dual media filters. This might be achievable by performing studies with three or more columns working in parallel and combining the conditions described in this document (inlet flow rate, filtration rate, etc.) during an extended period of time.

Also, it is important to state that during the experiments, the samples that were taken in the anthracite layer were not analyzed. This might be interesting in order to study the removal efficiency of heavy metals through the anthracite layer, since high percentage of HM removal was obtained in the experiments. This will help to elucidate the adsorption and/or cation exchange capacity of the filter material and for other materials as well.

In conclusion, the feasibility of these type of filtration systems (dual media filtration) is almost unthinkable due to its inherent operational costs. For example, if this filters were to be assembled for a WWTP with 20.000 inhabitants-equivalent, the amount of sand and anthracite will be enormous bearing excessive costs not only to buy these materials (in a weekly/monthly basis?) but also to dispose them (incineration, proper landfills), since we are dealing with hazardous materials.

Nevertheless this project shows that these type of techniques are more suitable for small scale plants or even home-use.

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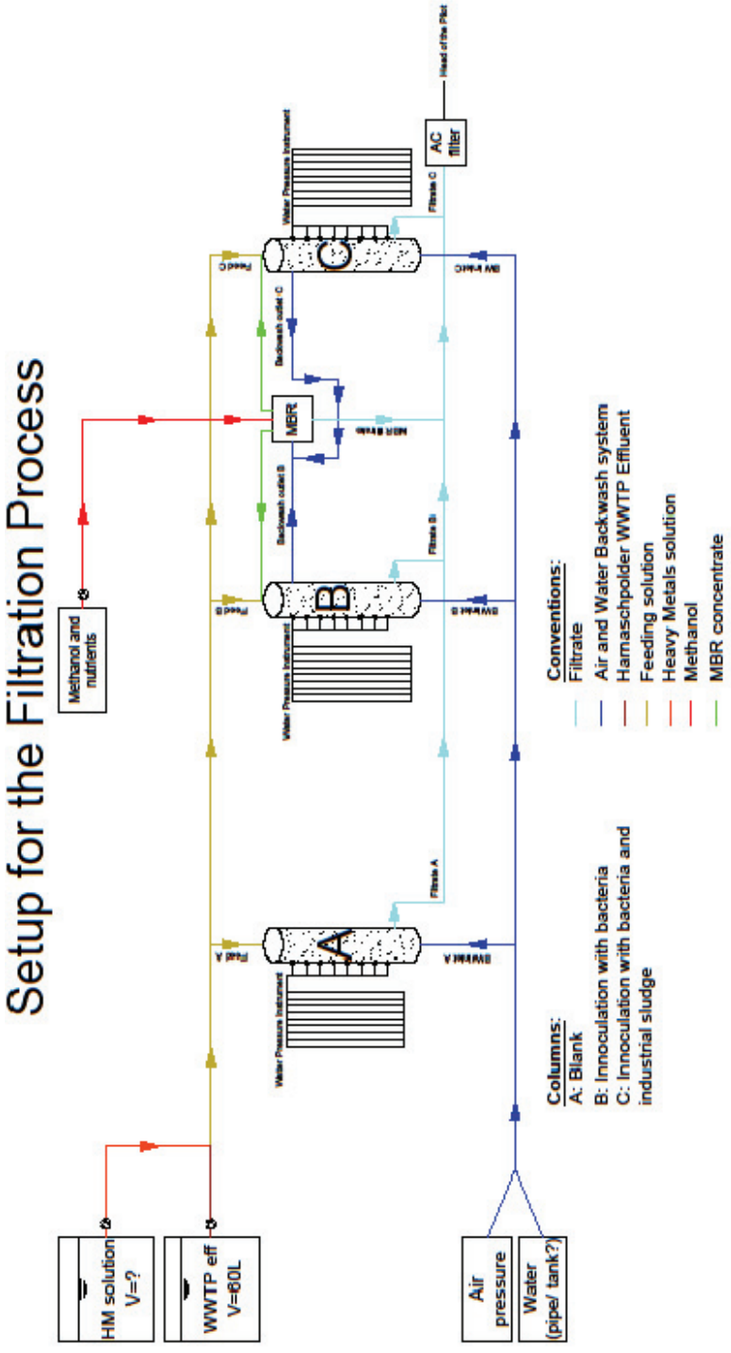
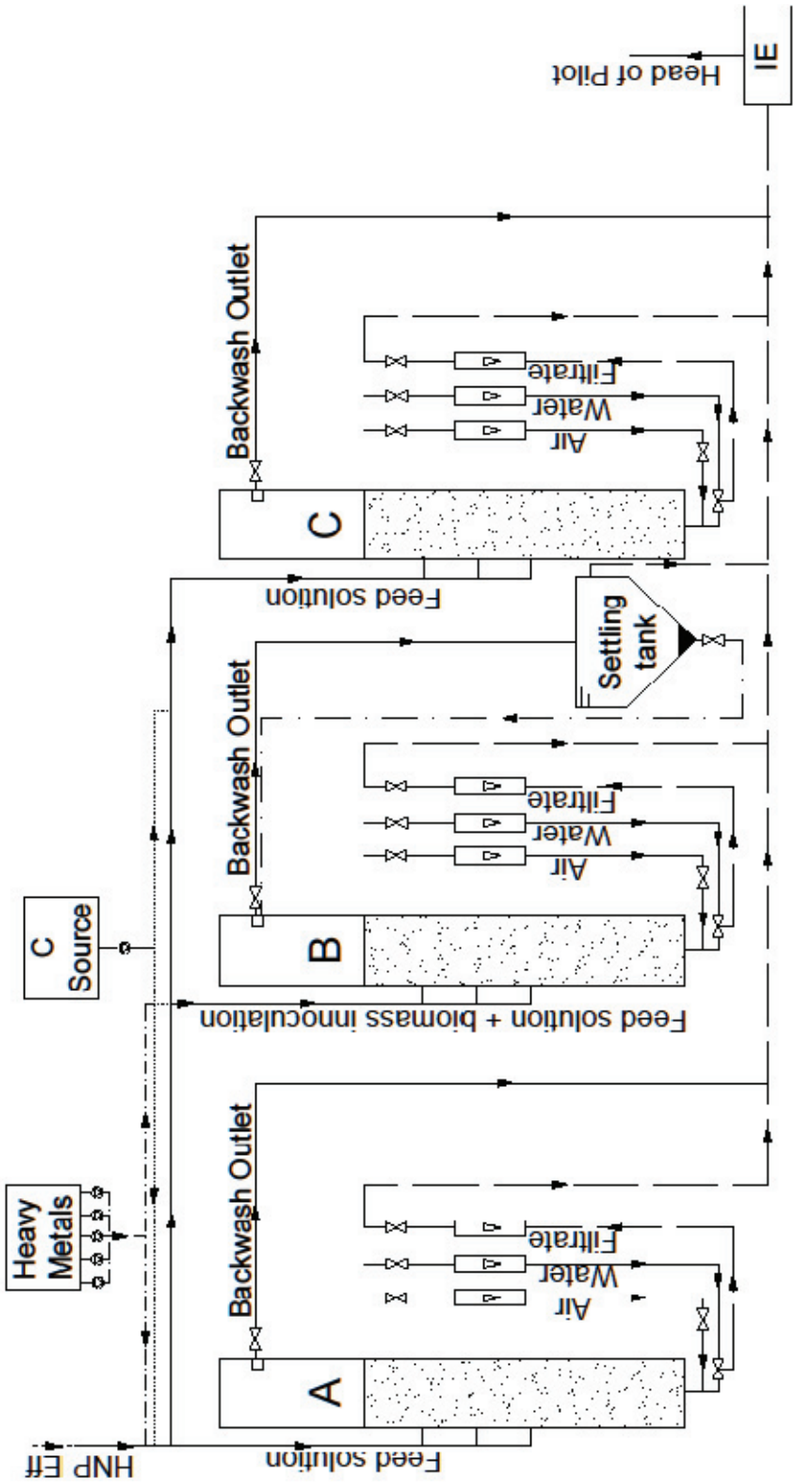
APPENDIXES

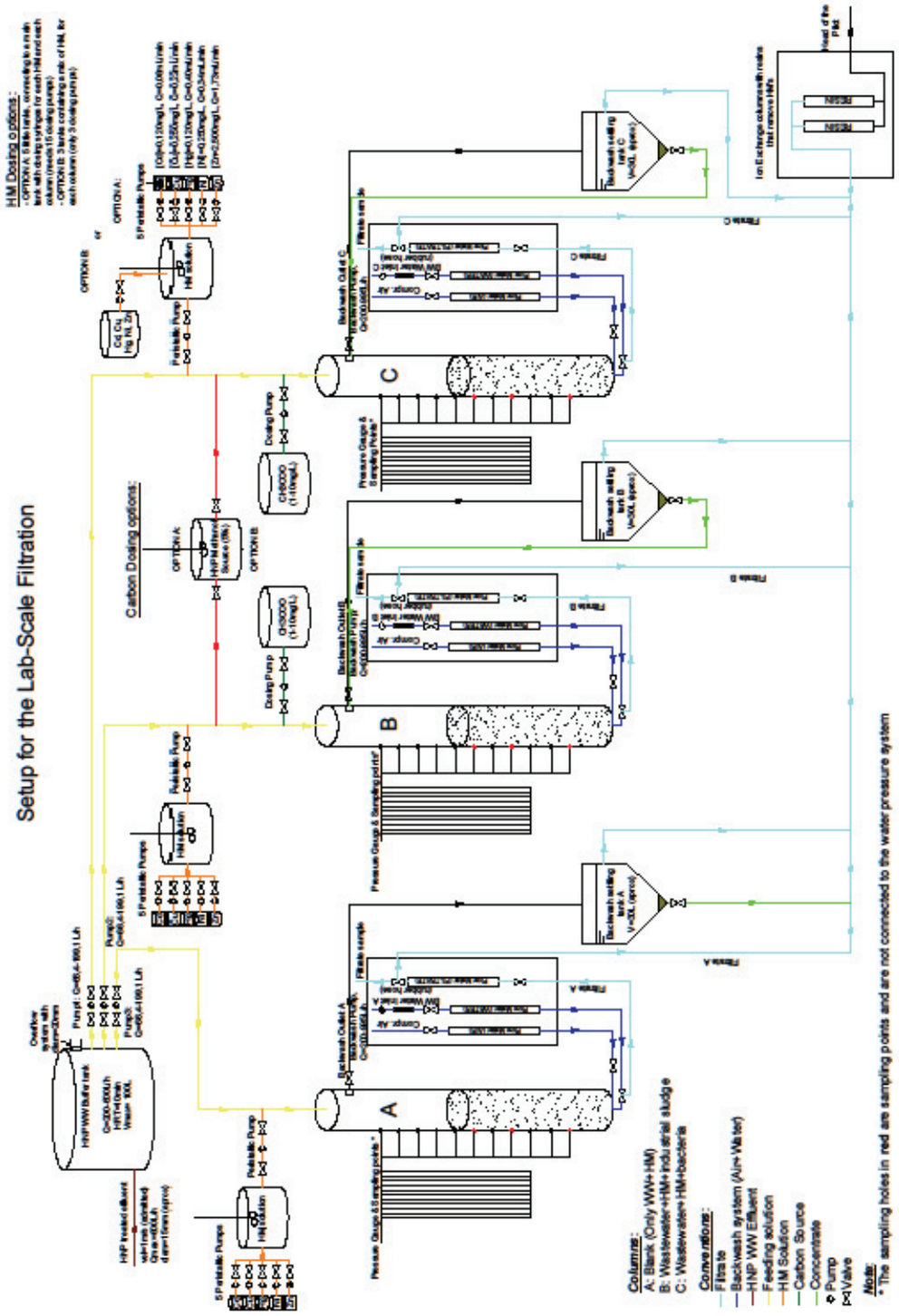
Appendix I. Filter Design



Appendix II. Filter Design – Detailed Setup



Appendix III. Filter Design – Detailed Setup (2)



Appendix IV. Filter «start-up» manual

– Filter Start-up

1) First of all, the filter must be assembled according to the schematics of the lab-scale sand filtration;

2) The next step is filling all the three filters with 1,5m of sand with a specific porosity of 1.4-2.0mm;

3) All the outlet valves of the filter must be closed before filling the filters;

4) After the valves are closed, the filter must be charged with filtered water (or clean water, if available). The water must be introduced from the bottom until the whole bed is covered enough (about 0,1m above the top sand layer) in order to prevent being scoured or disturbed by turbulence from the admission of the WWTP water;

5) Open the effluent control valve in the bottom, to release the filtered water at a filtration rate of one fourth of the design rate (about 1-5 m/h).

6) For a best operation of the filters during the experience, it is recommended to perform an early test with three different velocity rates for each filter (e.g. 5-10-15 m/h) with just water;

7) It is also recommendable to perform a backwash test for each column, with three different backwashing velocity rates using plain water (e.g. 15-45-75 m/h) and also varying backwash times. The following steps explain the procedure to backwash the filters:

   i) Turn on the air compressor, check the air pressure on the manometer next to the instruments and clean the filter for 1.5minutes (just air). Turn on the valve that connects to the settling tanks;
   ii) After 1.5minutes cleaning with just air, turn on the water (the valve connected to a garden hose) and let it clean for 1 minute. The backwash flow must be set between 200-995 L/h;
   iii) After cleaning the filter with air and water, turn off the air compressor on the main switch and then close the air valve on the bottom of the filter;
   iv) Keep the water running for just 30 more seconds to complete the backwash cycle. The filter should appear clean by this time.
   v) In this early stage, the backwash water should not be very dirty which makes the settling tanks dispensable.

8) After these initial tests are complete, the filters must be emptied, cleaned and filled again with fresh water, repeating the step 4).

9) When the backfilling is complete, the backfilling valve must be closed to start filling the filter with the feeding solution (treated wastewater, heavy metals, bacteria and nutrients);

10) Fill the three columns until the desired working level for the supernatant is reached;

11) The feeding of the filter must be interrupted so that the two columns can be inoculated (column B: industrial sludge only, column C: selected bacteria and industrial sludge). There are two possibilities for inoculating the filters: using a syringe (100mL or bigger) to inject the bacteria and nutrient solution directly on top of the filter or at different heights (using the several sampling holes) or just simply pour the solution directly on top of the column, using a bottle or other container;

12) In this early stage, it is important to enable the settling of the biological layer in the filter. During this stage the filtration rate should be minimal at the beginning of the experience and gradually increased from time to time. To check the settling of the biofilm in the two filters (the first column is the blank), chemical and bacteriological analyses of both raw water and filtrate (TSS, TOC, SVS, COD, etc.) must be executed with a periodicity of a week;

13) In the early stage of the experience, the backwash cannot be done otherwise it will compromise the settling of the biofilm. In addition, the valves that connect the three settling tanks must be closed until the first backwash is done.

Appendix V. Filter operation manual

1) After the biofilm is settled on the entire filter medium (this in this case is the sand), the experimental phase can take place. The pump is turned on and the feeding rate is adjusted by the appropriate valve to the desired flow, best suited for the experiment (between 66.4-199.1 L/h). The feeding is carried out 24 hours a day;

    i) The feeding concentrations can be adjusted by increasing or decreasing the flow of each HM dosing pump;

2) As the filtration mechanism takes place, the filtrate will exit the column from the bottom and goes directly into the ion exchange columns, prior to the disposal of the water;

3) The backwash system for the three filters must be done with a periodicity of 24h, according to previous experiments and it last only 2-3minutes. This is just simple a starting point, because during the whole experience the backwash should be adjusted according to the clogging of the filter. On the three filters different backwash velocity rates can be tested by simply closing or opening the valve;

    i) To perform a backwash, please run the step 7) on the «Filter Start-Up»;
    ii) During the entire backwash, the dirty water must go directly to the settling tanks to remove suspended solids and to concentrate biomass. When the backwash is complete, the valves that connect to the settling tanks must be closed instantly;
    iii) After some hours, open slightly the purge valve and carefully extract the concentrate so that it can be reintroduced back into the system.

4) The determination of certain parameters such as heavy metals and water quality, on both influent and effluent, should be done at least once a week as following:

    i) Collection of samples from the feeding solution (for each column) should be taken in order to analyze the following parameters: pH, TSS, SVS, COD, TOC and both dissolved and total metals using FAAS and/or X-ray diffraction analysis;
    ii) The effluent solution – the filtrate – should also be analyzed according to the same parameters as the previous solution. The samples can be taken by simply opening the valve located at the bottom of the filter, and pouring some solution into a sampling vessel. The filtrate must also be subjected to a bacterial count;
    iii) For a more thorough analysis samples should be taken from the existing sampling points of the columns, located at different heights for a better perception of the working conditions.

Appendix VI. Results of the filter experiments

Operation phase	Run Time (Tr)	Heavy metal	Mother solution (ug/L)		Filter A - no bacteria						Filter B - with CH34					
					Influent (ug/L)		Effluent (ug/L)		Anthracite layer (ug/L)		Influent (ug/L)		Effluent (ug/L)		Anthracite layer (ug/L)	
	(days)		Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total
HM without MeOH	0	Cd	381050	388340	330	360	56	50			330	360	56	87		
		Cu	328900	331800	270	290	96	92			260	290	81	100		
		Ni	351800	358400	350	340	240	240			340	340	220	270		
		Zn	328000	332000	380	330	95	88			320	330	93	110		
	3	Cd	382410	378570	310	320	270	250			260	260	240	230		
		Cu	326900	321800	250	260	210	200			220	210	170	180		
		Ni	352200	343500	330	320	310	290			370	250	250	240		
		Zn	328000	323000	360	310	220	260			240	270	210	210		
HM with MeOH	0	Cd	358960	368670	280	280	180	180	240	240	250	260	250	210	250	250
		Cu	309700	319300	220	230	120	120	170	170	200	220	190	150	180	180
		Ni	329100	336300	270	270	210	210	250	250	240	250	290	250	250	250
		Zn	309000	316000	260	260	130	120	390	210	230	240	190	140	220	220
	2	Cd	366350	365570	270	270	280	280	270	280	270	270	270	270	260	270
		Cu	320900	324800	220	230	200	200	200	210	220	220	200	200	200	210
		Ni	329600	329400	260	250	260	250	250	260	250	250	250	240	250	250
		Zn	320000	320000	300	300	270	260	270	260	260	260	450	300	290	260

Appendix VII. Cadmium input file

```
DATABASE llnl.dat

USER_GRAPH
-headings pH Cd(OH)2
-chart_title «Cadmium Equilibrium»
-axis_scale x_axis 5 13 0.5
-axis_scale y_axis 0 500 50
-axis_scale sy_axis 1 5 1
-axis_titles «pH» «Cd (ug/L)»
-initial_solutions false
-start
10 graph_x – la(«H+»)
20 graph_y tot(«Cd»)*112.4e6
-end


SOLUTION 1
    temp      19
    pH        6.52
    pe        4
    redox     pe
    units     mmol/l
    density   1.023
    Cl        137 charge
    Cr        3.5 ug/l
    Cu        3.67 ug/l
    Hg        0.15 ug/l
    Fe        195 ug/l
    Ni        9.8 ug/l
    Pb        8.2 ug/l
    Zn        30 ug/l
    As        1.57 ug/l
    C(4)      2.23 mMol/l
    O(0)      20
    Na        96.6
    Mg        8.56
    S(6)      62.5
    K         23
    Ca        63.6
    N(5)      4.7
    N(-3)     0.58
    P(5)      0.49
    Cd        400 ug/L

SOLUTION 2 Heavy metals solution
    temp      15
    pH        7
    pe        4
    redox     pe
    units     mmol/l
    density   1.023
    Cd        0.005
    Cl        0.01
    -water    1 # kg

SOLUTION 3
    MIX 1 HM+WW
    1 0.50
    2 0.50

REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Cd(OH)2 0.0 0 precipitate_only
END

USER_GRAPH
-headings pH CdCO3 (Otavite)

USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Otavite 0.0 0 precipitate_only
END
```

```
USER_GRAPH
-headings pH CdS

USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
CdS 0.0 0 precipitate_only
END
```

```
USER_GRAPH
-headings pH Cd3(PO4)2

USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Cd3(PO4)2 0.0 0 precipitate_only
END
```

Appendix VIII. Copper input file

```
DATABASE llnl.dat

USER_GRAPH
-headings pH CuS (Covellite)
-chart_title «Copper Equilibrium»
-axis_scale x_axis 5 13 0.5
-axis_scale y_axis 0 450 50
-axis_scale sy_axis 1 5 1
-axis_titles «pH» «Cu (ug/L)»
-initial_solutions false
– start
10 graph_x – la(«H+»)
20 graph_y tot(«Cu»)*63.546e6
-end

SOLUTION 1
    temp      19
    pH        6.52
    pe        4
    redox     pe
    units     mmol/l
    density   1.023
    Cl        137 charge
    Cr        3.5 ug/l
    Cd        3.67 ug/l
    Hg        0.15 ug/l
    Fe        195 ug/l
    Ni        9.8 ug/l
    Pb        8.2 ug/l
    Zn        30 ug/l
    As        1.57 ug/l
    C(4)      2.23 mMol/l
    O(0)      20
    Na        96.6
    Mg        8.56
    S(6)      62.5
    K         23
    Ca        63.6
    N(5)      4.7
    N(-3)     0.58
    P(5)      0.49
    Cu        400 ug/L

SOLUTION 2 Heavy metals solution
    temp      15
    pH        7
    pe        4
    redox     pe
    units     mmol/l
    density   1.023
    Cu        0.005
    Cl        0.01
    – water   1 # kg

SOLUTION 3
    MIX 1 HM+WW
    1 0.50
    2 0.50

REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Covellite 0.0 0 precipitate_only
END

USER_GRAPH
-headings pH Cu3(PO4)2

USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Cu3(PO4)2 0.0 0 precipitate_only
END
```

```
USER_GRAPH
-headings pH Cu3(CO3)2(OH)2

USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Azurite 0.0 0 precipitate_only
END
```

```
USER_GRAPH
-headings pH Cu2CO3(OH)2

USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Malachite 0.0 0 precipitate_only
END
```

Appendix IX. Nickel input file

```
DATABASE llnl.dat
USER_GRAPH
-headings pH NiCO3
-chart_title «Nickel Equilibrium»
-axis_scale x_axis 5 13 0.5
-axis_scale y_axis 0 450 50
-axis_scale sy_axis 1 5 1
-axis_titles «pH» «Ni (ug/L)»
-initial_solutions false
– start
10 graph_x – la(«H+»)
20 graph_y tot(«Ni»)*58.6934e6
-end

SOLUTION 1
    temp      19
    pH        6.52
    pe        4
    redox     pe
    units     mmol/l
    density   1.023
    Cl        137 charge
    Cr        3.5 ug/l
    Cd        3.67 ug/l
    Hg        0.15 ug/l
    Fe        195 ug/l
    Cu        9.8 ug/l
    Pb        8.2 ug/l
    Zn        30 ug/l
    As        1.57 ug/l
    C(4)      2.23 mMol/l
    O(0)      20
    Na        96.6
    Mg        8.56
    S(6)      62.5
    K         23
    Ca        63.6
    N(5)      4.7
    N(-3)     0.58
    P(5)      0.49
    Ni        400 ug/L

SOLUTION 2 Heavy metals solution
    temp      15
    pH        7
    pe        4
    redox     pe
    units     mmol/l
    density   1.023
    Ni        0.005
    Cl        0.01
    – water   1 # kg

SOLUTION 3
    MIX 1 HM+WW
    1 0.50
    2 0.50

REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
NiCO3 0.0 0 precipitate_only
END
USER_GRAPH
-headings pH Ni(OH)2

USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Ni(OH)2 0.0 0 precipitate_only
END
USER_GRAPH
-headings pH Ni2P2O7
USE SOLUTION 1
REACTION
```

```
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Ni2P2O7 0.0 0 precipitate_only
END
USER_GRAPH
-headings pH Ni3(PO4)2
USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Ni3(PO4)2 0.0 0 precipitate_only
END
USER_GRAPH
-headings pH NiS
USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Millerite 0.0 0 precipitate_only
END
```

Appendix X. Zinc input file

```
DATABASE llnl.dat
USER_GRAPH
-headings pH ZnCO3
-chart_title «Zinc Equilibrium»
-axis_scale x_axis 5 13 0.50
-axis_scale y_axis 0 450 50
-axis_scale sy_axis 1 5 1
-axis_titles «pH» «Zn (ug/L)»
-initial_solutions false
– start
10 graph_x – la(«H+»)
20 graph_y tot(«Zn»)*65.39e6
-end

SOLUTION 1
    temp      19
    pH        6.52
    pe        4
    redox     pe
    units     mmol/l
    density   1.023
    Cl        137 charge
    Cr        3.5 ug/l
    Cd        3.67 ug/l
    Hg        0.15 ug/l
    Fe        195 ug/l
    Cu        9.8 ug/l
    Pb        8.2 ug/l
    Ni        30 ug/l
    As        1.57 ug/l
    C(4)      2.23 mMol/l
    O(0)      20
    Na        96.6
    Mg        8.56
    S(6)      62.5
    K         23
    Ca        63.6
    N(5)      4.7
    N(-3)     0.58
    P(5)      0.49
    Zn        400 ug/L

SOLUTION 2 Heavy metals solution
    temp      15
    pH        7
    pe        4
    redox     pe
    units     mmol/l
    density   1.023
    Zn        0.005
    Cl        0.01
    – water   1 # kg

SOLUTION 3
    MIX 1 HM+WW
    1 0.50
    2 0.50

REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Smithsonite 0.0 0 precipitate_only
END

USER_GRAPH
-headings pH ZnS

USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Sphalerite 0.0 0 precipitate_only
END

USER_GRAPH
-headings pH Zn(OH)2
```

```
USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
Zn(OH)2(gamma) 0.0 0 precipitate_only
END

USER_GRAPH
-headings pH ZnCO3.H2O
```

```
USE SOLUTION 1
REACTION
NaOH 1
20 mmol in 100 steps
EQUILIBRIUM_PHASES 1
ZnCO3:H2O 0.0 0 precipitate_only
END
```